

# JOURNAL OF THE CHEMICAL SOCIETY.

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AND

## ANALYTICAL CHEMISTRY.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
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### PART I.

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#### Organic Chemistry.

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**Tautomeric Atomic Groupings.** By CONRAD LAAR (*Ber.*, 1901, 34, 3516—3521).—A theoretical paper unsuitable for abstracting.  
W. A. D.

**Production of Ethylene from Inorganic Sources.** By SAMUEL A. TUCKER and HERBERT R. MOODY (*J. Soc. Chem. Ind.*, 1901, 20, 971—972).—Calcium carbide with water evolves only acetylene, and aluminium carbide gives methane. It was hoped that on treatment of a mixture of these carbides ethylene might be formed, but only acetylene and methane were found in the evolved gas. Barium silicide with water evolves hydrogen and if this be intimately mixed with barium carbide the hydrogen so formed acts on the acetylene and ethylene is produced. The mixture is obtained by heating in an electric furnace witherite, silica, and coke, and the gas produced by the action of water contains up to 15 per cent. of ethylene. On replacing the barium mixture by a corresponding strontium or calcium mixture, the proportion of ethylene formed sinks to 5 per cent. in the former case and 2 per cent. in the latter.  
J. McC.

**Reactions of Nitrosyl Chloride and Nitrosates.** By WLADIMIR N. IPATIEFF and A. A. SOLONINA (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 496—501. Compare Abstr., 1900, i, 3 and 14).—From the results of previous experiments, Ipatieff concluded (*loc. cit.*) that unsaturated compounds containing either of the complexes :C:CH· or :C:C· readily

yield crystalline nitrosates and compounds with nitrosyl chloride, whilst with other unsaturated compounds possessing the structure  $\text{CH}:\text{CH}_2$ ,  $\text{CH}:\text{CH}$ , or  $\text{C}:\text{CH}_2$  this is not the case. It has, however, since been found by Prilejaeff that *isobutylene*, which contains the complex  $\text{C}:\text{CH}_2$ , also forms a crystalline product with nitrosyl chloride. This behaviour Ipatieff considers as probably due to the presence of two methyl groups, as in his own experiments with compounds containing this complex the carbon atom was combined with two different radicles. To obtain further information on this question, the authors have studied the behaviour of *isobutylene*,  $\psi$ -butylene, *diisobutylene*,  $\delta$ -methylheptylene, and a hydrocarbon obtained from dipropylethylcarbinol.

On passing dry *isobutylene* into strongly cooled amyl nitrite and slowly adding concentrated hydrochloric acid to the solution, the *oxime* of *chloroisobutaldehyde*,  $\text{CMe}_2\text{Cl}:\text{NOH}$ , is obtained in crystals melting at  $96-97^\circ$ ; on heating with sulphuric acid, it yields the chloroaldehyde which reduces Fehling's solution and ammoniacal silver oxide solution.

By the action of nitric acid on a solution of *isobutylene* in amyl nitrite and acetic acid, crystalline *isobutylene nitrosate* melting at  $114-115^\circ$  is obtained; when gently warmed with alcoholic potassium cyanide, it gives a *cyanide*,  $\text{CN}\cdot\text{CMe}_2\cdot\text{CH}:\text{NOH}$ , which melts at  $92-93^\circ$  and on hydrolysis yields an acid which was not investigated.

$\psi$ -Butylene gives no crystalline nitrosate or compound with nitrosyl chloride.

$\delta$ -Methyl- $\gamma$ -heptylene (1-methylpropyl-2-ethylethylene) yields a crystalline compound with nitrosyl chloride,  $\text{CMePr}^a\text{Cl}:\text{CEt}:\text{NOH}$ , melting at  $61-62^\circ$  and a crystalline *nitrosate*,  $\text{NO}_3\cdot\text{CMePr}^a\cdot\text{CEt}:\text{NOH}$ , melting at  $108-109^\circ$ .

The hydrocarbon of the formula  $\text{C}_9\text{H}_{18}$ , obtained by acting on ethyldipropylcarbinol with bromine and reducing the dibromo-derivative thus formed by means of zinc dust and alcohol, and which must be either  $\gamma$ -propyl- $\beta$ -hexylene or  $\delta$ -ethyl- $\gamma$ -heptylene, gives a crystalline *chloro-oxime*,  $\text{C}_9\text{H}_{18}\text{ONCl}$ , melting at  $81-83^\circ$  and a crystalline *nitrosate*,  $\text{C}_9\text{H}_{18}\text{O}_4\text{N}_2$ , melting at  $92^\circ$ .

T. H. P.

**Transformation of Alcohols into Unsaturated Hydrocarbons by the Action of Oxalic Acid.** By NICOLAI D. ZELINSKY and J. ZELIKOW (*Ber.*, 1901, 34, 3249-3256).—Pinacoline alcohol, when heated at  $100-110^\circ$  with anhydrous oxalic acid, yields a mixture of tetramethylethylene and another unsaturated hydrocarbon boiling at  $65-67^\circ$  and having a sp. gr. 0.6956 at  $19/4^\circ$ . *cyclo*Hexanol and 3-methyl-*cyclo*-1-hexanol, when heated with anhydrous or hydrated oxalic acid, furnish tetrahydrobenzene and methyl-*cyclo*hexene respectively. Menthol under these conditions yields menthene. *r*-Borneol, when heated at  $120-130^\circ$  with hydrated oxalic acid, yields a hydrocarbon,  $\text{C}_{10}\text{H}_{16}$ , which becomes solid at  $0^\circ$ , melts at  $3-4^\circ$ , and boils at  $155-160^\circ$ ; it has  $[\alpha]_D$   $8.12^\circ$ , and a sp. gr. 0.8622, and  $n_D$  1.4656 at  $25^\circ$ . When this experiment is repeated with anhydrous oxalic acid, two terpenes are produced boiling respectively at  $160-161^\circ$  and  $165-167^\circ$ ; these substances are inactive and do not solidify at  $0^\circ$ ;

the isomeride of lower boiling point has a sp. gr. 0.8579, and  $n_D$  1.4658 at 21°, the other hydrocarbon having a sp. gr. 0.8607 and  $n_D$  1.4700 at 20°; the respective mol. refractions are 43.9 and 44.14, the calculated value in each case being 43.53.

*l*-Borneol, when heated at 120—130° with crystallised oxalic acid, yields an inactive terpene boiling at 156—157° under 750 mm. pressure; the product has a sp. gr. 0.8545 and  $n_D$  1.4620 at 26°, the mol. refraction being 43.74.

The *hydrocarbon*,  $C_8H_{14}$ , derived from 1:3-dimethylcyclo-3-hexanol boils at 126—127° under 750 mm. pressure and has a sp. gr. 0.8015 and  $n_D$  1.4466 at 22° with a mol. refraction 36.61; it has  $[\alpha]_D$  95°.

The *hydrocarbon*,  $C_9H_{16}$ , obtained from 1-methyl-3-ethylcyclo-3-hexanol boils at 147—150° under 743 mm. pressure; it has a sp. gr. 0.8087 and  $n_D$  1.4514 at 25°, the mol. refraction being 41.3. The compound has  $[\alpha]_D$  56.8°.

The *hydrocarbon*,  $C_{11}H_{20}$ , produced from 1:3-dimethyl-4-isopropylcyclo-3-hexanol, boils at 180—182° under 753 mm. pressure and has  $[\alpha]_D$  88.53°; the sp. gr. and  $n_D$  at 26° are 0.8192 and 1.4561 respectively, the observed and calculated values of the mol. refraction being 50.43 and 50.24.

*Methylfenchene*,  $C_{11}H_{18}$ , prepared from methylfenchyl alcohol,  $C_{11}H_{20}O$ , boils at 172—173° under 743 mm. pressure, it has  $[\alpha]_D$  19.68°, a sp. gr. 0.8638 and  $n_D$  1.4643 at 27°, the values of the observed and calculated mol. refraction being 47.97 and 48.14 respectively. This hydrocarbon is the first representative of the methylated terpenes having the general formula  $C_{11}H_{18}$ . G. T. M.

**Pyrogenetic Reactions and Syntheses by means of the Electric Current.** By WALTHER LÖB (*Zeit. Elektrochem.*, 1901, 7, 903—921).—When a wire is heated to redness by an electric current in the vapour of boiling chloroform, hydrochloric acid and tetrachloroethylene are the principal products of decomposition at comparatively low temperatures, hexachlorobenzene and hexachloroethane and chlorine appearing also at higher temperatures. The tetrachloroethylene is probably formed by polymerisation of dichloromethylene which is the primary product of the decomposition. This view is supported by the following observations. The gases evolved yield small quantities of carbon monoxide when passed through water. A mixture of chloroform and water vapour yields much carbon monoxide. A mixture of chloroform and aniline vapours yields triphenylguanidine.

Carbon tetrachloride, when treated in the same way, yields the same products as chloroform with the exception of hydrochloric acid. In admixture with other substances, it also exhibits the same behaviour, so that primary decomposition into dichloromethylene and chlorine is assumed. Tetrachloroethylene yields hexachlorobenzene as principal product and smaller quantities of hexachloroethane. The primary products appear, therefore, to be dichloroacetylene and chlorine, the former yielding hexachlorobenzene by polymerisation. Hexachloroethane yields tetrachloroethylene and chlorine. T. E.

**Pyrogenetic Contact Reactions of Organic Compounds.** By WLADIMIR N. IPATIEFF (*Ber.*, 1901, **34**, 3579—3589. Compare Abstr., 1901, i, 248).—When alcohol vapour is passed through a heated tube it decomposes mainly in two different ways, a portion being converted into ethylene and water, whilst the remainder forms aldehyde and hydrogen. A portion of the aldehyde then decomposes into carbon monoxide and methane, this decomposition being more complete as the temperature becomes higher. In a glass tube at 700°, very little decomposition occurs, but at 800—830°, about one-fifth of the alcohol decomposed is converted into ethylene and water, whilst four-fifths yield hydrogen and acetaldehyde. About one-third of the aldehyde is further decomposed into carbon monoxide and methane. In a platinum tube, a similar decomposition occurs, but at a lower temperature, about six-sevenths of the alcohol decomposed being converted into hydrogen and aldehyde, or the products of its decomposition. In presence of zinc, the decomposition occurs at a considerably lower temperature, the zinc remains unchanged, and the proportion of the ethylene decomposition to the aldehyde decomposition varies with the condition of the metal. When rods of zinc are used at 620—650°, very little ethylene is produced and the yield of aldehyde amounts to 80 per cent. of the alcohol decomposed, only a very small amount of secondary decomposition taking place. The amount of hydrogen formed is at the same time greatly increased. When zinc dust is employed at 550°, nearly half the alcohol is converted into ethylene and water and much of the latter is decomposed with evolution of hydrogen. Brass containing 33 per cent. of zinc gives a similar result to that obtained with zinc rods. A single experiment with ethyl ether passed over zinc at 750° also yielded ethylene, acetaldehyde, methane, and carbon monoxide, but the volume of methane is much greater than that of the carbon monoxide. Comparative experiments show that only metals which are easily oxidised and at the same time form easily reducible oxides, are capable of lowering the temperature of decomposition, and this may be explained by supposing that the primary action is decomposition into ethylene and water; the water then reacts with the metal forming free hydrogen and the metallic oxide, which is at once reduced by a second mol. of alcohol, water and acetaldehyde being formed. A. H.

**Some New Derivatives of *sec.*-Butyl Alcohol.** By JAMES F. NORRIS and ERIK H. GREEN [and, in part, B. R. RICKARDS and H. G. JOHNSON] (*Amer. Chem. J.*, 1901, **26**, 293—318).—The reduction of methyl ethyl ketone to *sec.*-butyl alcohol cannot be effected in acid or neutral solutions, but with alkaline reagents the alcohol is obtained in varying amounts. The best yields (in one case 74 per cent.) were obtained by the action of sodium on moist ethereal solutions, some dimethylpinacene being simultaneously produced. *sec.*-Butyl alcohol boils at 99·7—99·9° under 756 mm. pressure, has the sp. gr. 0·8078 at 20°/4° and 0·8226 at 0°/4°, and  $n_D$  1·3949 at 25·3°. Attempts were made to resolve the alcohol into optically active substances by means of various micro-organisms, but without success. *sec.*-Butyl chloride, obtained by the action of hydrogen chloride on the alcohol in

presence of zinc chloride, boils at  $67.3-67.8^\circ$ , has a sp. gr. 0.8707 at  $20^\circ/4^\circ$ , and  $n_D$  1.3953 at  $25.2^\circ$ . *sec.*-Butyl bromide, prepared by the action of phosphorus tribromide on the alcohol, boils at  $91.3^\circ$ , has a sp. gr. 1.2507 at  $25^\circ/4^\circ$ , and  $n_D$  1.4344 at  $25.25^\circ$ . *sec.*-Butyl acetate boils at  $111.5-112^\circ$  under 744 mm. pressure, has the sp. gr. 0.8648 at  $25^\circ/4^\circ$  and 0.8900 at  $0^\circ/4^\circ$ , and  $n_D$  1.3866 at  $25.3^\circ$ . The *propionate* boils at  $132-132.5^\circ$ , has a sp. gr. 0.8657 at  $20^\circ/4^\circ$ , and  $n_D$  1.3938 at  $25.19^\circ$ . The *isovalerate* boils at  $163-164^\circ$  under 752 mm. pressure and has a sp. gr. 0.8482 at  $20^\circ/4^\circ$ . *Di-sec.-butyl succinate* boils at  $255.5-256.5^\circ$  under 750 mm. pressure, has a sp. gr. 0.9735 at  $20^\circ/4^\circ$ , and  $n_D$  1.4238 at  $25.25^\circ$ . The *benzoate* boils at  $234.5-235.5^\circ$  under 757 mm. pressure and has a sp. gr. 0.9945 at  $25^\circ/4^\circ$ .

*Di-sec.-butyl (dimethyl- $\gamma$ -hexane)*,  $\text{CH}_2\text{Me}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{CH}_2\text{Me}$ , obtained by the action of sodium on *sec.*-butyl bromide, is a fragrant, mobile liquid, which boils at  $116-116.2^\circ$  under 750 mm. pressure, has the sp. gr. 0.7332 at  $0^\circ/4^\circ$  and 0.7165 at  $25^\circ/4^\circ$ , and  $n_D$  1.4038 at  $25.2^\circ$ . When it is heated with fuming nitric acid at  $100^\circ$ , a small quantity of a tertiary nitro-compound is produced.

Dimethylpinacone boils at  $205-205.7^\circ$  under 752 mm. pressure, has a sp. gr. 0.9529 at  $25^\circ/4^\circ$ , and  $n_D$  1.4521 at  $25.25^\circ$ , and when cooled solidifies to a mass of crystals melting at  $49^\circ$ ; both liquid and solid are optically inactive.

E. G.

**Dimethylpentadecylcarbinol and its Reaction with Bromine.** By WLADIMIR N. IPATIEFF and GRAVE (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 502—506).—In order to ascertain the influence of the mol. weight of an acid chloride on the yield of tertiary alcohol it gives when treated with an organo-zinc compound according to Butleroff's method, the authors have studied the action of zinc methyl (3 mols.) on palmityl chloride,  $\text{C}_{15}\text{H}_{31}\cdot\text{COCl}$  (1 mol.). A good yield of the resulting *dimethylpentadecylcarbinol*,  $\text{OH}\cdot\text{CMe}_2\cdot[\text{CH}_2]_{14}\cdot\text{CH}_3$ , was obtained. After purification by crystallisation from ether, this substance melts at  $34.5-35^\circ$  and is soluble in alcohol or benzene; it is volatile in a current of steam only to a very small extent, and gives the normal mol. weight by the cryoscopic method. The action of bromine on the alcohol gives an almost theoretical yield of a *dibromo*-derivative, which has a sp. gr. 1.162 at  $0^\circ/0^\circ$  and probably consists of a mixture of two isomerides, the main bulk being the compound having the formula  $\text{CMe}_2\text{Br}\cdot\text{CHBr}\cdot[\text{CH}_2]_{13}\cdot\text{CH}_3$ . By removing 1 mol. of hydrogen bromide from this dibromo-derivative, a liquid compound having a sp. gr. 0.922 at  $0^\circ/0^\circ$  is obtained, whilst heating it with alcoholic potassium hydroxide yields a *hydrocarbon*,  $\text{C}_{18}\text{H}_{34}$ , boiling at  $185-188^\circ$ . The latter is a transparent, faintly smelling liquid which has a sp. gr. 0.845 at  $0^\circ/0^\circ$  and decolorises bromine and potassium permanganate solutions; it is probably a tri-substituted allene of the constitution  $\text{CMe}_2\cdot\text{C}:\text{CH}\cdot\text{C}_{13}\text{H}_{27}$ . T. H. P.

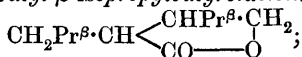
**Condensation of Higher Alcohols: Tricapryl Alcohol.** By WLADIMIR B. MARKOWNIKOFF and P. ZUBOFF (*Ber.*, 1901, 34, 3246—3249. Compare *J. Russ. Phys. Chem. Ges.*, 1889, 21, 129; Abstr., 1901, i, 182).—Capryl alcohol (methylhexylcarbinol), when heated at

190° with powdered sodium hydroxide, undergoes condensation accompanied by the elimination of water. The chief product is formed in accordance with the equation  $3C_8H_{18}O - 2H_2O = C_{24}H_{50}O$  and consists of a *secondary tricapryl alcohol*; this substance is a viscid, colourless liquid, lighter than water and boiling at 241—242° under 20 mm. and at 330° under the ordinary pressure; it yields a solid sodium derivative and when treated with valeryl chloride gives rise to a valerate. The compound seems to be alcoholic in character, for it readily condenses with phenylcarbimide, but does not interact with phenylhydrazine or ammoniacal silver nitrate; it is a saturated alcohol, and it only very slowly decolorises a chloroform solution of bromine. Small quantities of di- and tetra-capryl alcohols are produced during the condensation, the former of these compounds occurring in the oily fractions boiling at 220—225° under the ordinary pressure.

G. T. M.

**Dissociation of the Monatomic Alcohols, and their Ethers and Metallic Derivatives.** By JOHN U. NEF (*Annalen*, 1901, 318, 137—230. Compare Abstr., 1901, i, 626, and 1900, i, 4).—The alkylation of aniline by the sodium derivatives of the monohydric alcohols is explained by assuming that the latter substances undergo the alkylidene dissociation,  $CHRR'ONa = NaOH + >CRR'$ . The product always consists of the secondary amine and the yield is increased when aniline is replaced by its acetyl derivative. In this way, *isobutyl-* and *isoamyl-aniline* are readily obtained from the corresponding alkyl oxides. When acetylethylaniline and the sodium derivative of an alcohol are heated in sealed tubes, ethylaniline and a substituted acetic acid are produced. The result is explained in the following manner.  $>CRR' + CH_3 \cdot CO \cdot NEtPh = CHRR' \cdot CH_2 \cdot CO \cdot NEtPh$ ;  $CHRR' \cdot CH_2 \cdot CO \cdot NEtPh + NaOH = CHRR' \cdot CH_2 \cdot CO_2Na + NHEtPh$ . In this way, sodium ethoxide, *isobutyloxyde*, and *isoamyloxyde* give rise to *n*-butyric,  $\gamma$ -methylvaleric, and  $\delta$ -methylhexoic acids respectively. The formation of similarly substituted fatty acids does not occur with the formyl, propionyl, and butyryl derivatives of ethylaniline.

The sodium salt of  $\beta$ -hydroxymethyl- $\gamma$ -methyl- $\alpha$ -isobutylvaleric acid ( $\alpha$ -isobutyl- $\beta$ -isopropyl- $\gamma$ -hydroxybutyric acid;  $\gamma$ -hydroxyundecoic acid), obtained by heating sodium *isoamyl oxide* with formylethylaniline at 150—160°, is accompanied by ethylaniline and *isoamyl* and *decyl* alcohols. The free acid is an oil which yields a crystalline calcium salt,  $C_{22}H_{42}O_6Ca$ ; on distillation under diminished pressure, it loses water and passes into  $\alpha$ -isobutyl- $\beta$ -isopropylbutyrolactone,



this substance is a colourless oil with an agreeable odour; it boils at 144—145° under 12 mm. pressure, has a sp. gr. 0.965 at 23° and does not solidify at 15°.

*Isopropylisobutylsuccinic acid*,  $CO_2H \cdot CHPr^\beta \cdot CH(CH_2Pr^\beta) \cdot CO_2H$ , results from the oxidation of the lactone with an alkaline solution of potassium permanganate; it crystallises from water in needles and melts at 142°.

$\gamma$ -Methyl- $\alpha$ -isobutylvaleric acid ( $\alpha$ -isobutyl- $\beta$ -isopropylbutyric acid;



*undecic acid*),  $\text{CHMePr}^\beta \cdot \text{CH}(\text{CH}_2\text{Pr}^\beta) \cdot \text{CO}_2\text{H}$ , produced by reducing the lactone with fuming hydriodic acid and treating the impure iodo-undecic acid first produced with zinc dust and alcohol, is an oil boiling at  $145^\circ$  under 11 mm. pressure. The *chloride* boils at  $99^\circ$  under 13 mm. pressure and the *amide* melts at  $82-83^\circ$ .

$\delta$ -Methyl- $\alpha$ -isobutylhexic acid ( $\alpha$ -isobutyl- $\beta$ -isoamylacetic acid), produced by the ethyl malonate synthesis, boils at  $144-146^\circ$  under 13 mm. pressure; the *chloride* boils at  $100-102^\circ$  under 15 mm. pressure. The *amide* crystallises in transparent needles melting at  $84-85^\circ$ ; its melting point is depressed to  $65-68^\circ$  by the addition of the amide of the undecic acid, the two acids are therefore isomeric, not identical.

The decyl alcohol obtained in the formylethylaniline condensation is identical with the substance described by Borodin and Guerbet (Abstr., 1899, i, 471, 472). The author, in repeating the latter investigator's experiments, finds that when *isoamyl* alcohol and sodium *isoamyl*oxide are heated together in the absence of air the reaction does not commence below  $300-330^\circ$ , but that on passing dry air through the mixture condensation sets in at  $150-170^\circ$ , the products being the  $\text{C}_{10}$ -alcohol and valeric acid. This result is explained on the assumption that the initial phase of the reaction is the decomposition of the sodium derivative into sodium oxide, hydrogen, valeraldehyde, and the hypothetical *isoamylidene*,  $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH} <$ . The unsaturated hydrocarbon then alkylates the valeraldehyde, forming a  $\text{C}_{10}$ -aldehyde, which is subsequently reduced to the decyl alcohol. The constitution of the decyl alcohol is determined by comparing the derivatives of the corresponding decic acid with the analogous compounds of *isopropylisoamylacetic acid*; they are found to be identical.

$\delta$ -Methyl- $\alpha$ -isopropylhexic (*isopropylisoamylacetic acid*),  
 $\text{CH}_2\text{Pr}^\beta \cdot \text{CH}_2 \cdot \text{CHPr}^\beta \cdot \text{CO}_2\text{H}$ ,  
 obtained from ethyl *isopropylisoamylmalonate* (b. p.  $138-145^\circ$  under 14 mm. pressure), boils at  $135-136^\circ$  under 13 mm. pressure; the *chloride* boils at  $87^\circ$  under the same pressure; the *anilide* and *amide* crystallise in colourless needles melting respectively at  $105^\circ$  and  $112^\circ$ .

$\alpha\gamma$ -Decylglycol ( $\alpha$ -isobutyl- $\beta$ -isopropyltrimethylene glycol) [ $\epsilon$ -methyl- $\beta$ -isopropyl- $\alpha\gamma$ -hexylene glycol],  $\text{OH} \cdot \text{CH}_2 \cdot \text{CHPr}^\beta \cdot \text{CH}(\text{CH}_2\text{Pr}^\beta) \cdot \text{OH}$ , prepared by the action of powdered sodium hydroxide on valeraldehyde, boils at  $146-150^\circ$  under 30 mm. pressure and has a sp. gr. 0.92 at  $23^\circ$ ; this substance is accompanied by valeric acid and the substituted acraldehyde,  $\text{C}_{10}\text{H}_{18}\text{O}$ . The glycol, valeraldehyde, or *isoamyl* alcohol, when heated at  $280-300^\circ$  with potash-lime, yields valeric acid and hydrogen.

*Diisobutyl ketone*,  $\text{CO}(\text{CH}_2\text{Pr}^\beta)_2$ , results from the oxidation of valeraldehyde or the preceding glycol with chromic acid; it is an oil having an odour of peppermint and boiling at  $56^\circ$  under 11 mm. and at  $164-166^\circ$  under the ordinary pressure; the *oxime* is oily, boiling at  $114-116^\circ$  under 20 mm. pressure; the *semicarbazone* crystallises in needles and melts at  $106-107^\circ$ . Sodium *tert.*-amyloxide, when heated alone, yields methane, hydrogen, and a small quantity of  $\gamma$ -methyl- $\beta$ -butylene; in the presence of potash-lime, it gives rise

to methane, hydrogen, alkali carbonate and propionate, but not to amylene or any other olefine.

Benzophenone, when heated with sodium ethoxide, *isobutyl* oxide, or *isoamyl*oxide, yields benzhydrol and in the case of the second experiment this product is accompanied by a small amount of *aa-dimethyl-β-β-diphenylpropionic acid*,  $\text{CHPh}_2 \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$ ; the acid crystallises in colourless plates and melts at  $134-135^\circ$ . This result is explained by supposing that diphenylmethylenes,  $\text{Ph}_2\text{C} <$  (an alkylidene derived from benzophenone) combines with *isobutyric acid*.

A large portion of the communication is devoted to the decompositions occurring when the alcohols, ethers, aldehydes, and fatty acids are heated; these reactions are explained by assuming that the initial dissociations involve the production of alkylidenes. This part of the investigation cannot, however, be satisfactorily summarised.

G. T. M.

**Oxidation of Propylene Glycol by Oxidising Ferments.** By ANDRÉ KLING (*Bull. Soc. Chim.*, 1901, [iii], 25, 905-910).—Details of work already published (*Abstr.*, 1901, i, 625).

N. L.

**Structure of *iso*Butylene Chlorohydrin.** By K. KRASSUSKY (*J. pr. Chem.*, 1901, [ii], 64, 387-393).—A claim for priority (see *Abstr.*, 1901, i, 246; Michael, *ibid.*, 625).

R. H. P.

**Action of Mannitol on Bismuth Nitrate.** By LUDWIG VANINO and OTTO HAUSER (*Zeit. anorg. Chem.*, 1901, 28, 210-218).—Bismuth nitrate dissolves to a clear solution in an aqueous solution of mannitol and these solutions are more stable the greater the proportion of mannitol. When molecular proportions of bismuth nitrate and mannitol are employed, the compound  $\text{BiO} \cdot \text{NO}_3 \cdot \text{C}_6\text{H}_{14}\text{O}_6$  is obtained by adding alcohol and, after separating the mannitol which is precipitated, adding ether. It is sparingly soluble in water and easily so in potassium or sodium hydroxide.

The compound,  $\text{Bi}_2\text{O}_3 \cdot 2\text{C}_6\text{H}_{14}\text{O}_6$ , is obtained by allowing a solution of bismuth nitrate in mannitol to remain more than three months and then precipitating it with alcohol. It separates in yellowish-white, crystalline granules, is slightly soluble in water, easily so in potassium or sodium hydroxide, but insoluble in ammonia and barium hydroxide solution and is partially decomposed when dissolved in water.

The compound,  $\text{Bi}_2\text{O}_3 \cdot 4\text{C}_6\text{H}_{14}\text{O}_6 \cdot 3\text{H}_2\text{O}$ , crystallises from the filtrate obtained in the precipitation of the preceding compound, is a white powder easily soluble in water, has not the sweet taste of mannitol, and gradually decomposes on exposure to the air. When heated at  $130^\circ$ , it is converted into the compound  $\text{Bi}_2\text{O}_3 \cdot 4\text{C}_6\text{H}_{14}\text{O}_6$ , which is insoluble in water and easily soluble in potassium or sodium hydroxide.

The solution of bismuth nitrate in mannitol, since it contains no excess of acid, is very suitable for the preparation of bismuth salts by double decomposition. The authors have prepared the following salts from this solution, bismuth oxalate, citrate, gallate, salicylate, camphorate: the double salts with potassium chromate and dichromate, the tri-iodide, and a white, amorphous precipitate with borax.

E. C. R.

**Action of Zinc Methyl on Alcohols.** By S. A. TOLKATSCHIEFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 469—474).—Zinc ethoxide,  $\text{Zn}(\text{OEt})_2$ , is obtained, together with methane, as a white powder by the action of zinc methyl on ethyl alcohol in an atmosphere of carbon dioxide or, better, of nitrogen or hydrogen. The crude product contains a little zinc methyl ethoxide, from which it may be freed by heating with excess of ethyl alcohol. The ethoxide cannot be distilled, is insoluble in ordinary solvents, and readily absorbs moisture from the air.

*Zinc isobutyloxyde*,  $\text{Zn}(\text{O}\cdot\text{CH}_2\cdot\text{CHMe}_2)_2$ , prepared from zinc methyl and isobutyl alcohol, is a fine, white powder which is insoluble in the ordinary solvents. It cannot be distilled, and when heated it decomposes, the volatile products being mainly isobutylene, hydrogen, and isobutyl isobutyrate with smaller quantities of carbon monoxide and dioxide, saturated hydrocarbons, isobutaldehyde, and isobutyl alcohol; no isobutyl ether is obtained. A residue of 44 per cent. of the isobutyloxyde remains in the distilling flask as a porous, grey mass.

T. H. P.

**Glycerophosphorous Acid and Glycerophosphites.** By AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and F. PERRIN (*Compt. rend.*, 1901, 133, 643—644).—When phosphorus trichloride is slowly added to excess of cooled glycerol, hydrogen chloride is eliminated and a syrup obtained which contains the excess of glycerol, hydrochloric acid, and *glycerophosphorous acid*,  $\text{PHO}(\text{OH})\cdot\text{OC}_3\text{H}_5(\text{OH})_2$ . The *calcium* salt is obtained by dissolving the syrup in water, removing hydrogen chloride by moist silver oxide, and neutralising with calcium carbonate. After evaporation, addition of alcohol precipitates the salt as a white, crystalline, deliquescent powder. In aqueous solution, the acid rapidly hydrolyses, forming glycerol and phosphorous acid. Its salts, with the exception of the silver salt, are very soluble in water; the alkali salts are also soluble in alcohol.

K. J. P. O.

**Reducing Action of certain Nitro-derivatives.** By LÉO VIGNON and F. GERIN (*Compt. rend.*, 1901, 133, 540—542).—Methyl and ethyl nitrates and glycerol dinitrate and trinitrate have no reducing action on alkaline solutions of cupric salts. Erythritol tetranitrate has a slight reducing action and dulcitol hexanitrate a strong reducing action similar to that of the mannitol derivatives (compare Abstr., 1901, i, 662).

C. H. B.

**Nitro-derivative of Pentaerythritol.** By LÉO VIGNON and F. GERIN (*Compt. rend.*, 1901, 133, 590—592).—Pentaerythritol, when treated with fuming nitric acid and sulphuric acid, yields a *tetranitropentaerythritol* which forms colourless prisms melting at  $138-140^\circ$ , deflagrating if suddenly heated and detonating under a hammer. It is not affected by ordinary reducing agents and has no action on alkaline solutions of cupric salts, differing in this respect from erythritol tetranitrate (compare preceding abstract).

C. H. B.

**(Derived) Nitrates of Arabitol and Rhamnitol. Constitution of certain Ethereal Nitrates.** By LÉO VIGNON and F. GERIN (*Compt. rend.*, 1901, 133, 641—643. Compare preceding abstract).—*Arabitol penta-*

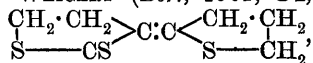
*nitrate*,  $C_5H_7(NO_3)_5$ , is prepared by treating arabitol with fuming nitric acid at  $-5^\circ$ , and precipitating the nitrate with sulphuric acid, and is obtained as a colourless, non-crystallisable syrup, which readily reduces alkaline cupric solutions. *Rhamnitol pentanitrate*,  $C_6H_9(NO_3)_5$ , is a syrup, also possessing energetic reducing properties. The view is expressed that the reducing properties are due to an oxidation of the primary alcohol group,  $\cdot CH_2\cdot OH$ , into the group  $\cdot CH(OH)_2$ ; the latter is then converted by nitrous acid into the group  $\cdot CH(OH)\cdot ONO$ , which, under the influence of alkalis, yields aldehyde and nitrite,  $\cdot CH(OH)\cdot ONO + KOH = KNO_2 + H_2O + \cdot CHO$ , and thus reduces Fehling's solution. The oxidation of the primary alcohol group only occurs when at least two  $\cdot CH\cdot NO_3$  groups are present in the molecule. K. J. P. O.

**Product of Condensation of Butyric Acid.** By GIACOMO ALBO (*Arch. Sci. phys. nat. Genève*, 1901, [iv], 12, 339—346).—On distilling commercial butyric acid, a fraction, boiling at  $158-160^\circ$ , was obtained which, when kept for two months exposed to light, deposited a white, gelatinous solid. This substance,  $C_{13}H_{22}O_8$ , is a tribasic acid, which was only obtained as an amorphous powder melting at  $220^\circ$ . The silver salt,  $C_{13}H_{19}O_8Ag_3$ , prepared from an ammoniacal solution of the acid and silver nitrate, is amorphous; a green copper salt and a barium salt were also prepared. K. J. P. O.

**Action of Zinc on a Mixture of Ethyl Acetoacetate with Methyl or Ethyl Iodide.** By SERGIUS N. REFORMATSKY and N. LUKASCHWITSCH (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 436—447).—The action of zinc and ethyl acetoacetate on either methyl or ethyl iodide yields a crystalline compound of the composition  $C_{12}H_{19}O_6IZn$ ; with the former iodide, the gaseous product consists of methane with a small proportion of hydrogen, whilst in the case of ethyl iodide, ethane and hydrogen are evolved. The author considers all the possible formulæ for the crystalline compound mentioned, and comes to the conclusion that it has the structure  $IZnO\cdot CMe\cdot CH\cdot CO_2Et, C_6H_{10}O_3$ . The reaction takes place in the following three stages: (1)  $Zn + MeI = ZnMeI$ , (2)  $OH\cdot CMe\cdot CH\cdot CO_2Et + ZnMeI = IZnO\cdot CMe\cdot CH\cdot CO_2Et + CH_4$ , (3)  $IZnO\cdot CMe\cdot CH\cdot CO_2Et + C_6H_{10}O_3 = IZnO\cdot CMe\cdot CH\cdot CO_2Et, C_6H_{10}O_3$ .

On passing dry ammonia through a cooled ethereal solution of this compound, a white, microcrystalline precipitate of the formula  $C_9H_{38}O_3N_7I_4Zn_2$  separates out; it is insoluble in organic solvents, but is dissolved and decomposed by mineral acids. No definite product could be obtained with aniline or phenylhydrazine. T. H. P.

**Trithiodibutyrolactone.** By FRITZ WEIGERT (*Ber.*, 1901, 34, 3386—3405).—Trithiodibutyrolactone,

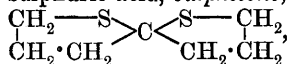


was prepared by Gabriel and Day (*Abstr.*, 1890, 1249) by the action of alcoholic potassium hydrogen sulphide on  $\gamma$ -chlorobutyronitrile, and crystallises in large, red tablets of the triclinic system [ $a:b:c = 0.736921:1:0.803146$ ;  $\alpha = 125^\circ 23' 40''$ ;  $\beta = 95^\circ 5' 16''$ ;  $\gamma = 93^\circ 15' 52''$ ]. It melts at  $116^\circ$  and does not decompose at  $180^\circ$ . It unites with

chlorine and bromine, forming unstable compounds, and with iodine gives a *derivative*,  $C_8H_{10}I_2S_3$ , which separates out as a dark red, crystalline powder and melts and decomposes at  $136^\circ$ . With bromoacetic acid, it yields a thetine *derivative*,  $C_8H_{10}S_3 \cdot CH_2Br \cdot CO_2H$ , which crystallises in small, yellow needles melting at  $154.5-155^\circ$ . Trithiodibutylolactone yields a *hydrazone*,  $C_8H_{10}S_2 \cdot N_2H_2$ , which forms large crystals melting at  $104.5^\circ$ , and also an *oxime*,  $C_8H_{10}S_2 \cdot NOH$ , which crystallises in stellate groups of needles or rhombohedral tablets, sinters at  $197^\circ$  and melts and decomposes at  $201-202^\circ$ . On reduction, the thiolactone is converted into *bistetramethylene sulphide*,

$\begin{array}{c} CH_2-S \\ | \quad | \\ CH_2 \cdot CH_2 \end{array} > CH \cdot CH < \begin{array}{c} CH_2 \cdot S \\ | \quad | \\ CH_2 \cdot CH_2 \end{array}$ , which is a light yellow, viscid, unpleasant smelling oil, and boils at  $300.7^\circ$ . The corresponding *sulphone*,  $C_8H_{14}O_4S_2$ , crystallises in six-sided tablets melting at  $145-146^\circ$ .

When boiled with baryta water, the thiolactone yields a *mercaptothionic acid*,  $OH \cdot C_8H_{10}S_2 \cdot SH$ , which, however, very readily loses water and reforms the original compound. The dibenzoyl derivative, *mercaptothiondibenzoic anhydride*,  $C_{22}H_{20}O_3S_3$ , crystallises in colourless plates melting at  $91-92^\circ$ . When the crude mercaptothionic acid is heated with dilute sulphuric acid, *sulphetone*,



is formed as a light yellow oil which has the sp. gr. 1.1557 at  $17.5^\circ$ , and boils at  $230-260^\circ$ . It does not react with hydrazine or hydroxylamine and is not affected by reducing agents. On oxidation, it yields *sulphonetone*,  $C_7H_{12}O_4S_2$ , which crystallises in rhombohedral forms, melts at  $164^\circ$ , and can be sublimed. Sulphetone appears to be the

sulphur analogue of the oxetone,  $\begin{array}{c} CH_2-O \\ | \quad | \\ CH_2 \cdot CH_2 \end{array} > C < \begin{array}{c} O-CH_2 \\ | \quad | \\ CH_2 \cdot CH_2 \end{array}$ , of Fittig and Ström (*Annalen*, 1890, 256, 57), and it is from the formation of this compound that the constitution of the trithiodibutylolactone has been deduced.

The thiolactone is converted by hydrogen peroxide into a *compound*,  $C_8H_{10}OS_3$ , which crystallises in orange-yellow needles melting at  $134.5^\circ$ . Benzoyl chloride converts the thiolactone into a *compound*,  $C_{15}H_{13}ClS_3$ , which crystallises in matted, lemon-yellow, hygroscopic needles melting at  $227^\circ$ . This substance behaves as the chloride of a base, and other salts can be prepared from it, although the free base has not been isolated. The *platinichloride*,  $(C_{15}H_{13}ClS_3)_2PtCl_4$ , forms yellow needles; the *nitrate* melts at  $218^\circ$ ; the *bromide* crystallises in needles, and melts and decomposes at  $267^\circ$ ; the *iodide* melts at  $275^\circ$ ; and the *thiocyanate* melts and decomposes at  $212^\circ$ . *p*-Nitrobenzoyl chloride yields an analogous *derivative*,  $NO_2 \cdot C_6H_4 \cdot C_9H_8ClS_3$ , which melts at  $210^\circ$ , and forms an *iodide* melting at  $242^\circ$ . Acetyl chloride also appears to act in a similar manner, but the chloride has not been obtained pure. The *thiocyanate*,  $C_{10}H_{11}S_3 \cdot SCN$ , crystallises in slender needles and melts at  $175^\circ$ .

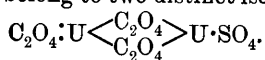
A. H.

**Oxalouranous Compounds.** By VOLKMAR KOHLSCHÜTTER (*Ber.*, 1901, 34, 3619-3635. Compare *Abstr.*, 1901, i, 448).—Uranous

oxalate,  $U_2(C_2O_4)_4$  (*loc. cit.*), yields an acid oxalate,  $U_2(C_2O_4)_2 \cdot H_2C_2O_4 \cdot 8H_2O$ , in the form of a white powder, which is readily converted back into the green compound on treatment with water or dilute acids.

*Trioxalodiuuranous chloride*,  $U_2(C_2O_4)_3Cl_2 \cdot 12H_2O$ , obtained when uranous oxalate is dissolved in concentrated hydrochloric acid and the solution kept over sulphuric acid, forms glistening, colourless needles which turn pink when heated at  $100^\circ$ . All the uranium is not deposited from the solution in the form of the chloride, and if the crystals are kept too long in contact with the mother liquor they re-dissolve. Water decomposes the chloride, hydrogen chloride being liberated.

A *sulphate*,  $U_2(C_2O_4)_3SO_4 \cdot 12H_2O$ , obtained when the solution of the chloride is cooled and treated with dilute sulphuric acid, forms greyish-green, minute needles, and cannot be obtained by treating the chloride with sulphuric acid. It is suggested that the chloride and sulphate belong to two distinct isomeric series, for example,  $C_2O_4(U \cdot C_2O_4 \cdot Cl)_2$  and



*Oxalouranous sulphate*,  $U_2C_2O_4(SO_4)_2 \cdot 6H_2O$ , is formed when uranous oxalate is boiled with dilute sulphuric acid, and crystallises in dark olive-green, flat prisms. When the urano-oxalate is dissolved in concentrated sulphuric acid, it yields *uranous sulphate*,  $U(SO_4)_2 \cdot 4H_2O$ , a colourless powder readily decomposed by water; a *sulphate*,  $U(SO_4)_2 \cdot 2H_2O$ , has also been obtained in the form of grey needles. *Diuranous sulphate*,  $U_2(SO_4)_4 \cdot 8H_2O$ , is formed when a solution of the compound,  $U(SO_4)_2 \cdot 4H_2O$ , in dilute sulphuric acid is evaporated, and is identical with Hillebrand and Melville's sulphate. *Potassium uranous sulphate*,  $U(SO_4)_2 \cdot K_2SO_4 \cdot 2H_2O$ , crystallises in glistening, green plates. *Ammonium uranous sulphate*,  $U(SO_4)_2 \cdot 4(NH_4)_2SO_4 \cdot 3H_2O$ , forms deep green, glistening pyramids. *Potassium uranotetraoxalate*,  $U_2(C_2O_4)_4(C_2O_4)_4 \cdot K_8 \cdot 10H_2O$ , obtained by precipitating a solution of urano-oxalate in potassium oxalate with alcohol, is a colourless, minutely crystalline compound, and its solution is not oxidised on evaporation.

The *barium salt*,  $U_2(C_2O_4)_4(C_2O_4)_4Ba_4 \cdot 12H_2O$ , forms reddish-violet needles, and when warmed at  $105^\circ$  turns green. *Potassium diuranohexaoxalate*,  $U_2(C_2O_4)_4(C_2O_4)_3K_6 \cdot 8H_2O$ , crystallises in green prisms. *Potassium diuranopentaoxalate*,  $U_2(C_2O_4)_4K_2C_2O_4 \cdot 8H_2O$ , is a greyish-green, crystalline powder. Oxalothorium chloride,  $Th_2(C_2O_4)_3Cl_2 \cdot 9H_2O$ , obtained by the action of concentrated hydrochloric acid on thorium oxalate, crystallises in flat prisms, and is decomposed when boiled with water. The action of various salts, alkali carbonates, sulphates, and arsenates on uranous oxalate has been studied. The relationship between the colour and constitution of the urano-oxalates is also discussed.

J. J. S.

**Formation of Carbon Rings.** By A. KÖTZ and P. SPEISS (*J. pr. Chem.*, 1901, [ii], 64, 394—400).—A preliminary account of researches on the formation of carbon rings by the action of dihaloids on disodium derivatives of the esters of methylene- and other dicarboxylic acids.

The action of methylene di-iodide on ethyl ethanetetra-carboxylate

yields a colourless *oil*,  $C_{15}H_{22}O_8$ , which boils at  $155-160^\circ$  under 12 mm. pressure and is not identical with the ester obtained by Perkin by the action of iodine on ethyl disodiumethylenedimalonate. The ethylene dihaloids have no action on ethyl disodioethanetetracarboxylate, but trimethylene dibromide interacts with it, forming ethyl *cyclopentane-tetracarboxylate*.  
R. H. P.

**Bromomalonic Dialdehyde.** By ROBERT LESPIEAU (*Compt. rend.*, 1901, 133, 538—540).—The compound,  $C_3H_3O_3Br$ , obtained by the action of excess of bromine on many compounds containing  $C_3$ , such as dibromoallyl methoxide,  $CHBr:CHBr \cdot CH_2 \cdot OMe$ , or bromoallyl alcohol,  $CHBr:CH \cdot CH_2 \cdot OH$ , or its methyl ester, is *bromomalonic dialdehyde*; it melts and decomposes at  $140^\circ$ , is very soluble in water or organic solvents, and can be crystallised from benzene. Its aqueous solution yields a reddish-violet coloration with ferric chloride, a green precipitate with cupric acetate, a violet coloration with Fischer's reagent, and a coloration with magenta decolorised by sulphurous acid. With potassium carbonate, it yields a crystalline derivative,  $CKBr(CHO)_2$ , and with phenylhydrazine it forms Balbiano's 1-phenyl-4-bromopyrazole.  
C. H. B.

**Interaction of Formaldehyde and Acetylacetone.** By LUDWIG KNORR and PAUL RABE (*Ber.*, 1901, 34, 3489—3490).—Formaldehyde interacts with acetylacetone in dilute alkaline solution, yielding about 14 per cent. of a heavy *oil*,  $C_8H_{10}O_2$ , boiling at  $200-201^\circ$ , which slowly deposits crystals of the same composition melting at  $32^\circ$ . The oil instantaneously decolorises bromine and is more rapidly attacked than acetylacetone by alkaline potassium permanganate; it combines with phenylhydrazine at  $140-150^\circ$ , giving a *derivative*,  $C_{14}H_{16}ON_2$ , which boils at  $220-225^\circ$  under 30 mm. pressure.  
W. A. D.

**The Oxycelluloses.** By A. NASTUKOFF (*Ber.*, 1901, 34, 3589—3591. Compare Abstr., 1901, i, 315).—Cellulose yields 90 per cent. of  $\beta$ -oxycellulose when it is heated for an hour on the water-bath with about 2.5 parts of nitric acid of sp. gr. 1.3. This fact destroys the value of the theory of the constitution of cellulose founded by Cross and Bevan (*Trans.*, 1883, 43, 22) on their observation that only 30 per cent. of  $\beta$ -oxycellulose could be obtained from cellulose.

The barium salt of  $\beta$ -oxycellulose contains, according to two analyses, 4.9 and 5.8 per cent. of barium, corresponding with the mol. weights 1353 and 1104, on the assumption that the substance is a monobasic acid. The barium salt of  $\gamma$ -oxycellulose, on the other hand, only contains about 1 per cent. of barium, corresponding with a molecular weight of nearly 7000. The salts of the  $\beta$ -oxycelluloses are hard, whilst those of the  $\gamma$ -oxycelluloses are brittle; they also differ in their behaviour when heated and when their solutions are evaporated.

A. H.

**Dimethylethanolamine.** By LUDWIG KNORR and HERMANN MATTHES (*Ber.*, 1901, 34, 3482—3484).—Ethylene oxide readily combines completely at the ordinary temperature with dimethylamine in presence of a little water to form dimethylethanolamine [dimethylhydroxyethyl-

amine] (compare Abstr., 1899, i, 461); to prepare the latter, however, in the anhydrous state, it is necessary to heat the dry ingredients for 40 hours at 150°. Thus obtained, it boils at 13·5° (corr.) under 758 mm. pressure, has a sp. gr. 0·8866 at 20°/4°,  $\mu_D$  1·430 at 20°, and a mol. refraction 25·93 (calc. 26·08). The *picrate* (with  $\frac{1}{2}$ H<sub>2</sub>O) crystallises in stout needles and when dry melts at 96—97°; the *picrolonate* crystallises from dilute alcohol in yellow needles and melts and decomposes at 197°.

W. A. D.

**Ethyl Bromo- and Chloro-aminocrotonates.** By ROBERT BEHREND and HERMANN SCHREIBER (*Annalen*, 1901, 318, 371—381. Compare Abstr., 1900, i, 210).—This is chiefly an account of work already published. Hofmann's process for the preparation of acetyl-bromoamide does not give a very good yield of this product, but when acetamide is dissolved in well cooled bromine and the mixture treated with a concentrated solution of potassium hydroxide (1 : 1), 40—55 per cent. of the theoretical amount is obtained.

G. T. M.

**Double Salts of Bismuth Thiocyanate and Potassium Thiocyanate.** By LUDWIG VANINO and OTTO HAUSER (*Zeit. anorg. Chem.*, 1901, 28, 219—222).—The *double salt*, Bi(SCN)<sub>3</sub>·3KSCN, is obtained by adding the calculated quantity of potassium thiocyanate to a solution of bismuth nitrate in mannitol and then precipitating the mannitol and potassium nitrate with alcohol and allowing the filtrate to crystallise at the ordinary temperature. It separates from alcohol in red crystals, is not hygroscopic, does not change on exposure to the air, and is decomposed by water into a yellowish, amorphous powder.

The *double salt*, Bi(SCN)<sub>3</sub>·9KSCN, is obtained in a similar manner to the preceding salt, a larger proportion of potassium thiocyanate being used; it crystallises in large, deep red crystals, is exceedingly hygroscopic, and decomposes at the ordinary temperature into a red compound mixed with sulphur and bismuth sulphide.

The ammonium double salts are obtained in the same manner, but cannot be purified.

E. C. R.

**The so-called isoAmides and True Amides.** By KARL AUWERS (*Ber.*, 1901, 34, 3558—3559).—Polemical; a reply to Hantzsch and Voegelen (Abstr., 1901, i, 676).

T. M. L.

**Action of Urethane on Pyruvic Acid.** By L. J. SIMON (*Compt. rend.*, 1901, 133, 535—538).—The direct action of urethane (ethyl carbamate) on pyruvic acid in the absence of any condensing agent yields *diurethanepyruvic acid*, CMe(NH·CO<sub>2</sub>Et)<sub>2</sub>·CO<sub>2</sub>H, a white, crystalline solid, which melts at 138—139°, readily remains in a state of superfusion, and decomposes before it volatilises. It is only slightly soluble in cold water and is hydrolysed in hot water, but dissolves in most organic solvents. It is a somewhat strong acid and can be titrated with either phenolphthalein or methyl-orange as indicator; the potassium and silver salts are crystallisable, and the zinc, barium, lead, and mercurous salts are soluble, but the mercuric and ferric salts are insoluble in water.

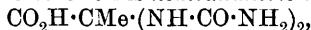
*Ethyl diurethanepyruvate*, obtained in the usual way from the acid or by the action of ethyl carbamate on ethyl pyruvate in presence of



hydrochloric acid, forms slender, white needles, which melt at  $109^{\circ}$  and can be recrystallised from boiling water. Diurethanepyruvic acid has none of the properties characteristic of ketones and does not give the pyruvic acid reaction with sodium nitroprusside; when boiled with water, it readily yields pyruvic acid and ethyl carbamate.

C. H. B.

**Action of Carbamide on Pyruvic Acid.** By L. J. SIMON (*Compt. rend.*, 1901, 133, 587—590).—In the production of homoallantoin by the action of carbamide on pyruvic acid as described by Grimaux, the first product of the reaction is *homoallantoic acid*,



which is readily obtained by the interaction of carbamide and pyruvic acid in the calculated proportion at the ordinary temperature in presence of water or alcohol. It is a white, microcrystalline solid, which begins to decompose at  $140^{\circ}$  without melting; it can be titrated with ordinary indicators, forms a crystallisable potassium salt, the aqueous solution of which yields no precipitates with solutions of metallic salts. The ethyl ester is crystalline and decomposes at  $195$ — $200^{\circ}$  without melting. When heated for a long time with a small quantity of water, homoallantoic acid is almost completely converted into homoallantoin (pyruvil). The behaviour of carbamide with pyruvic acid is similar to that of urethane (preceding abstract).

Semicarbazide and pyruvic acid yield compounds analogous to the hydrazines. The ester,  $\text{CO}_2\text{Et}\cdot\text{CMe}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , is a white, crystalline compound, which melts and begins to decompose at  $204$ — $205^{\circ}$ ; it has been obtained in a different manner by Thiele and Bailey (*Abstr.*, 1899, i, 169). The corresponding acid decomposes without melting at about  $200^{\circ}$ .

C. H. B.

**Electrolytic Reduction of Cyclic Ureides.** By JULIUS TAFEL and LUDWIG REINDL (*Ber.*, 1901, 34, 3286—3291).—The electrolytic reduction of parabanic acid dissolved in 60—70 per cent. sulphuric acid yields a mixture of hydantoin and ethylenecarbamide, and that of dialuric acid affords hydrouracil, together with trimethylenecarbamide and a small quantity of a *substance*,  $\text{C}_4\text{H}_8\text{O}_2\text{N}_2$ , possibly  $\text{CO}\langle\text{NH}\cdot\text{CH}_2\rangle\text{CH}\cdot\text{OH}$ , melting between  $185^{\circ}$  and  $195^{\circ}$ .

Uramil is very susceptible to reduction, but yields principally amorphous products and only a small quantity of hydrouracil; alloxan also yields only a small proportion of hydrouracil together with some alloxantin and a large amount of non-crystalline material.

W. A. D.

**Oxidation of Benzene Hydrocarbons by means of Manganese Dioxide and Sulphuric Acid.** By H. FOURNIER (*Compt. rend.*, 1901, 133, 634—636).—When oxidised in the cold with manganese dioxide and sulphuric acid (sp. gr. = 1.53), *o*-xylene yields *o*-tolualdehyde, representing 37 per cent. of the calculated amount.  $\psi$ -Cumene is oxidised to the extent of 22 per cent. to *o*-xylaldehyde. Cymene yields only a small quantity of cuminaldehyde; ethylbenzene gives benzaldehyde and acetophenone (methyl phenyl ketone).

K. J. P. O.

**Action of Sodium Nitrite on 1-Chloro-2:4-dinitrobenzene and Picryl Chloride.** By OTTO KYM (*Ber.*, 1901, 34, 3311—3313).—1-Chloro-2:4-dinitrobenzene is converted quantitatively by sodium nitrite in dilute alcoholic solution at the ordinary temperature into sodium 2:4-dinitrophenoxide; the compound,  $C_6H_4(NO_2)_2 \cdot ONO$ , is probably the initial product, but could not be isolated. Nitrogen trioxide is without action on 1-chloro-2:4-dinitrobenzene in cold ethereal solution.

Sodium nitrite converts picryl chloride in cold acetone instantaneously into sodium picrate, but does not act on either *o*- or *p*-chloronitrobenzene.  
W. A. D.

**Preparation from *p*-Nitroaniline of Tri-, Tetra-, and Penta-iodobenzene and Allied Compounds.** By CONRAD WILLGERODT and EMIL ARNOLD (*Ber.*, 1901, 34, 3343—3354).—1:3:5-*Di-iodonitrobenzene*,  $C_6H_3I_2 \cdot NO_2$ , prepared by boiling diazotised 2:6-di-iodo-4-nitroaniline with alcohol, crystallises from alcohol in yellow needles and melts at 95—96°. 3:5-*Di-iodoaniline*,  $C_6H_3I_2 \cdot NH_2$ , crystallises in transparent needles and melts at 105°; the *sulphate* forms glistening, white flakes melting at above 200° with liberation of iodine, the *hydrochloride*, white needles decomposing without melting at above 200°, the *platinichloride*, yellow needles, and the *acetyl* derivative, small white needles melting at 101—102°. 1:3:5-Tri-iodobenzene,  $C_6H_3I_3$ , prepared from di-iodoaniline, crystallises from acetic acid in long, flexible needles, melts at 180°, and is identical with that prepared by Baeyer from iodoacetylene, and by Istrati.

1:2:3-Tri-iodo-5-nitrobenzene,  $C_6H_3I_3 \cdot NO_2$ , prepared from 2:6-di-iodo-4-nitroaniline, crystallises from alcohol in yellow needles, and melts at 105°. 3:4:5-Tri-iodoaniline,  $C_6H_3I_3 \cdot NH_2$ , crystallises from ether in white needles, melts at 78°, and can be distilled in a current of steam; the *sulphate* crystallises in white flakes and melts with decomposition when heated; the *hydrochloride* forms small needles and melts with decomposition when heated; the *platinichloride* forms reddish needles; the *acetyl* derivative crystallises in needles, and melts at 135°.

5:7-Di-iodoquinoline,  $C_9NH_5I_2$ , prepared by Skraup's method from 3:5-di-iodoaniline, crystallises from alcohol in white needles, sublimes when heated, and melts at 132°; the *methiodide* and *methochloride* melt with decomposition at above 250°.

5:6:7-Tri-iodoquinoline,  $C_9NH_4I_3$ , prepared from 3:4:5-tri-iodoaniline, crystallises from alcohol in white needles and melts at 102°.

1:2:3-Tri-iodobenzene,  $C_6H_3I_3$ , prepared from 3:4:5-tri-iodoaniline, crystallises from alcohol in white needles and melts at 86°; it is possibly identical with a tri-iodobenzene melting at 83—84° described by Istrati.

1:2:4:6-Tetraiodobenzene,  $C_6H_2I_4$ , crystallises from acetic acid or ether and melts at 148°.

2:6-Di-iodo-1:4-diaminobenzene,  $C_6H_2I_2(NH_2)_2$ , crystallises from hot water in needles, melts at 108°, and is readily oxidised to di-iodoquinone.

2:3:4:6-Tetraiodo-1:4-diaminobenzene,  $C_6I_4(NH_2)_2$ , prepared by the action of iodine chloride on the preceding compound, melts at 152°.

1:2:4:5 Tetraiodobenzene,  $C_6H_2I_4$ , prepared from the preceding

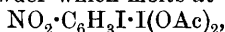
compound, crystallises from ether in white needles, sublimes when heated, and melts at 165°.

2 : 3 : 4 : 5-*Tetraiodoaniline*,  $C_6H_4 \cdot NH_2$ , prepared by the action of iodine chloride on 3 : 4 : 5-tri-iodoaniline, crystallises from alcohol in needles, melts at 92°, and becomes violet under the influence of light. 1 : 2 : 3 : 4-*Tetraiodobenzene*,  $C_6H_2I_4$ , crystallises from alcohol, sublimes when heated, and melts at 114°. Istrati has described two tetraiodobenzenes melting at 220° and 247°, whilst the three compounds now described melt at 148°, 165°, and 114°; as only three tetraiodobenzenes are possible, there must be an error awaiting discovery.

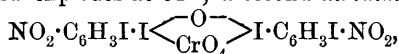
*Pentaiodobenzene*,  $C_6HI_5$ , from 2 : 3 : 4 : 5-tetraiodoaniline, forms white needles, crystallises from alcohol, sublimes when heated, and melts at 172°.

T. M. L.

**Derivatives of Symmetrical Di-iodonitrobenzene containing Polyvalent Iodine.** By CONRAD WILLGERODT and WALDEMAR ERNST (*Ber.*, 1901, 34, 3406—3416).—1-*Iodo-3-nitrophenyl 5-iodochloride*,  $NO_2 \cdot C_6H_3I \cdot ICl_2$ , obtained by passing chlorine into a warm (30°) acetic acid solution of *s*-di-iodonitrobenzene to which a little chloroform has been added, forms small, yellow needles; it is readily soluble in most organic solvents and when kept for some time parts with its chlorine. On treatment with 2 per cent. sodium hydroxide, or, even better, with warm sodium carbonate, it yields 1-*iodo-3-nitro-5-iodosobenzene* in the form of a pale yellow powder which melts at 118°. Its *acetate*,



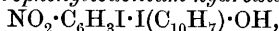
crystallises in colourless plates melting at 172°; its *basic sulphate*,  $(C_6H_3O_3NI_2)_2 \cdot H_2SO_4$ , melts and decomposes at 145° after turning dark coloured at 105°; the *basic nitrate*,  $NO_2 \cdot C_6H_3I \cdot I(OH) \cdot NO_3$ , is a white, amorphous powder, only sparingly soluble in water, and decomposes at 104°; the *basic chromate*,  $[NO_2 \cdot C_6H_3I \cdot I(OH)]_2CrO_4$ , is an orange-yellow powder and explodes at 81°; a second *chromate*,



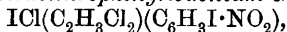
has been obtained by rubbing the iodoso-compound with a solution of chromium trioxide in acetic acid.

*Iodonitroiodoxybenzene*,  $NO_2 \cdot C_6H_3I \cdot IO_2$ , obtained by the action of sodium hypochlorite and a little acetic acid on the dichloride, is a pale yellow powder almost insoluble in water or acetic acid and exploding at 187°. Neither a tetrachloride nor a di-iodoxy-compound has been obtained.

*s*-*Iodonitrophenyl-phenyliodonium hydroxide*,  $NO_2 \cdot C_6H_3I \cdot IPh \cdot OH$ , has only been obtained in the form of a strongly alkaline, aqueous solution; the *chloride*,  $NO_2 \cdot C_6H_3I \cdot IPhCl$ , forms long, colourless needles, readily soluble in alcohol or chloroform and melting at 131°. The *bromide* melts at 211° and is insoluble in ether; the *iodide* is an amorphous powder melting at 152° and yields a *periodide*,  $NO_2 \cdot C_6H_3I \cdot IPhI_3$ , crystallising in red cubes and decomposing at 160°. The *dichromate*,  $[NO_2 \cdot C_6H_3I \cdot IPh]_2Cr_2O_7$ , forms orange-yellow needles which explode at 160°; the *nitrate* crystallises in yellow needles melting at 138°; the *platinichloride* is a yellowish-red powder which melts and decomposes at 197°, and the *mercurichloride* a flocculent precipitate melting at 198°.

*α-Naphthyl-s-iodonitrophenyliodonium hydroxide,*

obtained by shaking *α*-iodosonaphthalene and *s*-iodonitroiodoxybenzene with water and silver oxide, gives a strongly alkaline, aqueous solution; the *chloride* forms a white precipitate the *platinichloride* a flesh coloured powder melting at 178° the *bromide* melts at 168°, and the *iodide* melts and decomposes at 89°. The *dichromate* forms a reddish-yellow precipitate and explodes at 154°. *Iodonitrophenyldi-iodonitrophenyliodonium hydroxide*,  $\text{OH} \cdot \text{I}(\text{C}_6\text{H}_2\text{I}_2 \cdot \text{NO}_2)(\text{C}_6\text{H}_3\text{I} \cdot \text{NO}_2)$ , obtained as its sulphate by V. Meyer and Hartmann's method, has been converted into the following salts: the *chloride*, a flocculent precipitate, melting at 85°; the *bromide*, a yellow precipitate, melting at 101°; the *iodide*, which begins to decompose at 66° and is completely melted at 98°; the *dichromate*, exploding at 72°; the *platinichloride*, decomposing at 115°; and the *mercurichloride*, melting at 113°.

*Dichloroethyl-s-monoiodonitrophenyliodonium chloride,*

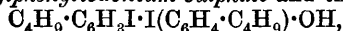
obtained from *iodonitrophenyliodochloride* and acetylene silver-silver chloride melts at 170°; the *bromide* melts at 159°, the *iodide* at 108°, the *nitrate* at 148°, the *dichromate* explodes at 107°, the *platinichloride* melts and decomposes at 162°, and the *mercurichloride* melts at 160°.

J. J. S.

**Derivatives of *p*-Iodotert.butylbenzene containing Polyvalent Iodine.** By CONRAD WILLGERODT and EBERHARD RAMPACHER (*Ber.*, 1901, 34, 3666—3678).—*p*-Iodotert.butylbenzene (Pahl, *Abstr.*, 1884, 1009) has been obtained from *p*-tert.butylaniline (Louis, *Ber.*, 1883, 16, 114) by Griess's reaction. It yields a *dichloride*,  $\text{C}_4\text{H}_9 \cdot \text{C}_6\text{H}_4 \cdot \text{ICl}_2$ , crystallising in sulphur-yellow needles, decomposing at 74° and readily soluble in chloroform but insoluble in light petroleum; the *dichloride* gives an *additive* compound with pyridine which melts at 124°.

*p*-Iodosotert.butylbenzene is a yellow powder decomposing at 189° and sparingly soluble in ether; the *acetate*,  $\text{C}_4\text{H}_9 \cdot \text{C}_6\text{H}_4 \cdot \text{I}(\text{OAc})_2$ , crystallises in large, transparent prisms melting at 95°. *p*-Iodoxytert.butylbenzene,  $\text{C}_4\text{H}_9 \cdot \text{C}_6\text{H}_4 \cdot \text{IO}_2$ , obtained by the action of sodium hypochlorite on the *dichloride*, is a colourless compound exploding at 201° and is readily soluble in acetic acid.

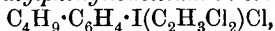
*Di-p*-tert.butylphenyliodonium hydroxide,  $\text{I}(\text{C}_6\text{H}_4 \cdot \text{C}_4\text{H}_9)_2 \cdot \text{OH}$ , has only been obtained in aqueous solution. The *chloride* is a colourless, micro-crystalline powder melting at 157° and is only sparingly soluble in hot water. The *bromide* melts at 144°; the *iodide*, obtained by Meyer and Hartmann's method (*Abstr.*, 1894, i, 242), is a yellow, amorphous powder melting and decomposing at 142°; it yields a *periodide*,  $\text{I}(\text{C}_6\text{H}_4 \cdot \text{C}_4\text{H}_9)_2 \cdot \text{I}_3$ , crystallising in dark brown needles and melting at 138°. The *nitrate* melts and decomposes at 142° and is only sparingly soluble in water. The *dichromate* decomposes at 105°, the *platinichloride* forms orange coloured plates melting and decomposing at 128—142°, and the *mercurichloride* crystallises in colourless prisms melting at 62°.

*Iododi-p*-tert.butylphenyliodonium sulphate and the hydroxide,

are both readily soluble in water. The *chloride* melts and decomposes at 94°, the *bromide* at 89°, the *iodide* at 86—87°, the *cyanide* readily decomposes, the *dichromate* melts at 118°, the *platinichloride* decomposes at 89°, and the *mercurichloride* melts at 56°. All the salts are comparatively unstable.

*Phenyl-p-tert.butylphenyliodonium chloride*,  $C_4H_9 \cdot C_6H_4 \cdot IPhCl$ , is crystalline and melts at 167°, the *bromide* melts at 157°, the *iodide* at 124°, the *nitrate* crystallises in colourless, glistening needles melting and decomposing at 141° and readily soluble in water or alcohol, the *dichromate* melts at 121°, the *platinichloride* begins to decompose at 152°, and the *mercurichloride* melts at 129°.

*Dichloroethyl-p-tert.butylphenyliodonium chloride*,



melts at 107°, the *bromide* crystallises in compact needles melting at 123°, the *iodide* melts at 91°, the *cyanide* rapidly decomposes, the *nitrate* melts at 126°, and the *dichromate* decomposes when removed from its mother liquor. The *picrate* melts at 158°, the *platinichloride* at 64°, and the *mercurichloride* at 73°.

J. J. S.

**Derivatives of p-isoAmylphenyl Iodide containing Polyvalent Iodine.** By CONRAD WILLGERODT and KURT DAMMANN (*Ber.*, 1901, **34**, 3678—3688).—Amino-p-isoamylbenzene is most readily obtained when aniline, isoamyl alcohol, and zinc chloride are heated in molecular proportion at 270—280° (compare Calm, *Abstr.*, 1882, 1284) and is purified by conversion into its sulphate. When diazotised and treated with potassium iodide solution, it yields p-iodoisoamylbenzene in the form of a colourless liquid distilling at 281° (corr.). The *dichloride*,  $C_5H_{11} \cdot C_6H_4 \cdot ICl_2$ , obtained by passing chlorine into a chloroform-acetic acid solution of the iodo-compound kept cool and well stirred, forms crystalline plates melting and decomposing at 84°, and readily soluble in benzene, ether, or chloroform; when kept, it gives up part of its chlorine. The *iodoso*-compound forms a snow-white powder melting and decomposing at 162° and is insoluble in water. The *acetate*,  $C_5H_{11} \cdot C_6H_4 \cdot I(OAc)_2$ , crystallises in long, colourless needles melting and decomposing at 78°. p-Iodoxyisoamylbenzene,  $C_5H_{11} \cdot C_6H_4 \cdot IO_2$ , after extraction with ether and 10 per cent. acetic acid, crystallises from hot water in glistening plates which explode at 200—203°.

*Di-p-isoamylphenyliodonium chloride*,  $I(C_6H_4 \cdot C_5H_{11})_2Cl$ , crystallises in needles melting at 74°; the *platinichloride* melts and decomposes at 178°, and the *mercurichloride* crystallises in plates decomposing at 163°. The *bromide* melts at 127°; the *iodide* melts at 68° and is converted into p-iodoamyl benzene. The *dichromate* decomposes at 137°.

*Phenyl-p-isoamylphenyliodonium chloride*,  $C_5H_{11} \cdot C_6H_4 \cdot IPhCl$ , crystallises in needles decomposing at 159°; the *platinichloride* is an orange coloured powder melting and decomposing at 165°, and the *mercurichloride* crystallises in glistening needles melting and decomposing at 132°. The *bromide* melts at 145°, the *iodide* melts at 118° and is at the same time decomposed into phenyl iodide and p-iodoamylbenzene; the *trichloroacetate* melts and decomposes at 85°, and the *nitrate* melts at 122°.

p-isoAmylphenyl- $\alpha$ -naphthyl-iodonium chloride,  $C_5H_{11} \cdot C_6H_4 \cdot I(C_{10}H_7)Cl$ , melts at 152°; the *platinichloride* melts and decomposes at 162°, and

the *mercurichloride* at  $141^{\circ}$ . The *bromide* melts at  $156^{\circ}$ , the *iodide* melts and decomposes at  $134^{\circ}$ , and the *dichromate* melts at  $74^{\circ}$  and explodes at  $90^{\circ}$ .

*p*-isoAmylphenyldichloroethylidonium chloride melts at  $132^{\circ}$ , the *bromide* melts and decomposes at  $109^{\circ}$ , and the *iodide* at about  $60^{\circ}$ . The *nitrate* crystallises in long, glistening needles and melts at  $82^{\circ}$ ; the *sulphate* melts and decomposes at  $56^{\circ}$ , and the *platinichloride* forms reddish-yellow crystals melting and decomposing at  $124^{\circ}$ .

J. J. S.

**Phenylated Naphthenes.** Phenylcyclohexane and its Derivatives. By NICOLAI KURSANOFF (*Annalen*, 1901, 318, 309—326. Compare Willstätter and Lessing, *Abstr.*, 1901, i, 265).—Phenylcyclohexane,  $C_6H_{11}Ph$ , prepared by adding cyclohexyl chloride to a cooled mixture of benzene and anhydrous aluminium chloride, melts at  $7^{\circ}$ , boils at  $239^{\circ}$  under 745 mm. pressure, and has a sp. gr. 0.9441 at  $20^{\circ}/0^{\circ}$ . The yield of this hydrocarbon decreases as the quantity of aluminium chloride employed increases. A higher fraction boiling at  $200$ — $315^{\circ}$  under 20—22 mm. pressure is also obtained in the preceding condensation; it yields a small quantity of a solid hydrocarbon, *o*-diphenylcyclohexane, crystallising from alcohol in needles and melting at  $170$ — $171^{\circ}$ ; the residual oil, when oxidised with dilute nitric acid, yields isophthalic acid, this result indicating that the liquid probably contains *m*-diphenylcyclohexane. The relative position of the phenyl radicles in *o*-diphenylcyclohexane is determined by preparing the hydrocarbon from pure *o*-dichlorocyclohexane.

Barium cyclohexylbenzenesulphonate,  $(C_6H_{11} \cdot C_6H_4 \cdot SO_3)_2Ba$ , produced by dissolving phenylcyclohexane in cold, fuming sulphuric acid, and converting the product into the barium salt, separates in anhydrous flakes which are sparingly soluble in cold water. The sodium and potassium salts are obtained in ill-defined crystals on adding the sulphonation product to concentrated solutions of the corresponding chlorides. The sulphonic acid, isolated by decomposing the lead salt with hydrogen sulphide, crystallises from mixtures of chloroform and benzene, or light petroleum, in slender needles and decomposes at  $114$ — $116^{\circ}$ ; it is probably a para-derivative.

*p*-Nitrocyclohexylbenzene,  $C_6H_{11} \cdot C_6H_4 \cdot NO_2$ , produced by adding phenylcyclohexane to fuming nitric acid (4—5 parts), crystallises from alcohol in well-defined prisms and melts at  $57.5$ — $58.5^{\circ}$ ; it is oxidised to *p*-nitrobenzoic acid when heated with dilute nitric acid for 60 hours.

*p*-Aminocyclohexylbenzene,  $C_6H_{11} \cdot C_6H_4 \cdot NH_2$ , obtained on reducing the corresponding nitro-compound with tin and hydrochloric acid, crystallises from light petroleum in leaflets melting at  $54$ — $56^{\circ}$ ; it is volatile in steam. The sulphate,  $(C_{12}H_{15} \cdot NH_2)_2H_2SO_4$ , crystallises in silky needles and decomposes at  $287$ — $290^{\circ}$ . The hydrochloride, hydrobromide, and nitrate crystallise in leaflets and decompose at  $261$ — $262^{\circ}$ ,  $280$ — $282^{\circ}$ , and  $225$ — $227^{\circ}$  respectively. The acetyl derivative,  $C_{12}H_{15} \cdot NHAc$ , and the thiocarbamide melt at  $128$ — $129.5^{\circ}$  and  $157$ — $158^{\circ}$  respectively.

*p*-cycloHexylbenzenediazonium sulphate,  $(C_6H_{11} \cdot C_6H_4 \cdot N_2)_2SO_4$ , results from the action of sodium nitrite on *p*-aminocyclohexylbenzene sulphate suspended in dilute sulphuric acid; it is only moderately soluble

in water, and when treated with an alkaline solution of  $\beta$ -naphthol yields the red azo-compound,  $C_6H_{11} \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH$ .

*p*-cycloHexylphenol,  $C_6H_{11} \cdot C_6H_4 \cdot OH$ , produced by heating a solution of the diazonium salt on the water-bath, crystallises from benzene or light petroleum in needles melting at  $132-133^\circ$ . This phenol is volatile in steam and only slightly soluble in water; its sodium and potassium derivatives dissolve but sparingly in water and are insoluble in solutions of the alkali hydroxides; the latter compound,  $C_6H_{11} \cdot C_6H_4 \cdot OK$ , crystallises in long needles.

Phenylcyclohexane reacts with bromine evolving hydrogen bromide, and when oxidised with nitric acid or potassium permanganate or dichromate yields benzoic acid. G. T. M.

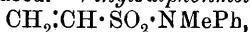
**Derivatives of Diphenyl.** By STEFAN VON NIEMENTOWSKI (*Ber.*, 1901, 34, 3325—3337).—Details are given of a method by which a 60 per cent. yield of 2:2'-dinitrodiphenyl may be obtained from *o*-nitroaniline, by the action of copper on the diazo-compound (compare Ullmann and Bielecki, *Abstr.*, 1901, i, 586); this substance is identical with the compound prepared by Täuber (*Abstr.*, 1891, 570) from dinitrobenzidine and is reduced by tin and hydrochloric acid to 2:2'-diaminodiphenyl. 2:2'-Diformylaminodiphenyl,  $C_{12}H_8(NH \cdot CHO)_2$ , crystallises from alcohol in stout crystals and melts at  $137^\circ$ . The dibenzoyl derivative,  $C_{12}H_8(NHBz)_2$ , crystallises from alcohol in stout crystals, softens at  $176^\circ$ , and melts at  $184^\circ$ . Carbonyl-2:2'-diaminodiphenyl,  $\begin{matrix} C_6H_4 \cdot NH \\ C_6H_4 \cdot NH \end{matrix} > CO$ , separates from glacial acetic acid in glistening crystals and melts at  $310^\circ$ .

2:2'-Diamino-4:4'-dimethyldiphenyl,  $C_{12}H_6Me_2(NH_2)_2$ , crystallises from alcohol in needles and melts at  $120^\circ$ . The diformyl derivative crystallises from alcohol in stout crystals or needles, softens at  $185^\circ$  and melts at  $187^\circ$ . The diacetyl derivative crystallises from alcohol in stout crystals or in needles and melts at  $189^\circ$ . The dibenzoyl derivative crystallises from alcohol in needles and melts at  $170^\circ$ . Carbonyl-2:2'-diamino-4:4'-dimethyldiphenyl crystallises from acetic acid in snow-white, woolly needles containing  $\frac{1}{2}$  mol.  $C_2H_4O_2$  and melts at  $339^\circ$ . The dibenzylidene derivative crystallises from acetic acid in yellow needles and melts at  $242^\circ$ . 2:7-Dimethylcarbazole,  $NH < \begin{matrix} C_6H_2Me \\ C_6H_3Me \end{matrix}$ , prepared from diaminodimethyldiphenyl by Täuber's method (*Abstr.*, 1893, i, 588), crystallises from alcohol and melts at  $283^\circ$ . 4:4'-Dimethyldiphenyleneoxide,  $O < \begin{matrix} C_6H_3Me \\ C_6H_3Me \end{matrix}$ , prepared by the method of Täuber and Halberstadt (*Abstr.*, 1892, 1470), crystallises from alcohol in glistening flakes and melts at  $82^\circ$ . T. M. L.

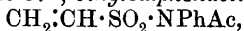
**Action of Nitrogen Trioxide and Peroxide on Stilbene.** II. By JULIUS SCHMIDT (*Ber.*, 1901, 34, 3536—3543. Compare *Abstr.*, 1901, i, 266).—Gabriel's 'stilbene dinitrite' (*Abstr.*, 1885, 1229) is identical with the *s*- $\alpha$ -diphenyldinitroethane described by the author (*loc. cit.*); the melting point given by Gabriel is incorrect. *s*- $\beta$ -Diphenyldinitroethane, formed along with stilbene nitrosite by the action of nitrous fumes on stilbene, crystallises from acetic acid in stout, white

prisms, melts at 150—152° to a yellow liquid, and decomposes at 200°; the  $\alpha$ - and  $\beta$ -compounds are related to one another in the same way as mesotartaric and racemic acids, and both yield the same tetraphenylpiperazine. T. M. L.

**Interaction of Aliphatic Disulphonic Chlorides and Aromatic Amino-compounds.** By WILHELM AUTENRIETH and P. RUDOLPH (*Ber.*, 1901, **34**, 3467—3482).—Ethylenedisulphonic chloride interacts with aniline (3 mols.) in benzene solution with elimination of sulphur dioxide (1 mol.) and hydrogen chloride (1 mol.) to form *vinylsulphanilide*,  $\text{CH}_2\text{:CH}\cdot\text{SO}_2\cdot\text{NHPh}$ , which crystallises in lustrous leaflets, melts at 68°, and, although an unsaturated compound, is not reduced by sodium amalgam, and does not combine with bromine. On hydrolysis with hydrochloric acid, it yields aniline and *isoethionic acid*, the latter being formed by the addition of  $1\text{H}_2\text{O}$  to the vinylsulphonic acid which is first produced. *Vinylsulphonmethylanilide*,



obtained either by the interaction of ethylenedisulphonic chloride and methylaniline or by methylating vinylsulphanilide, crystallises from dilute alcohol, melts at 79°, and is hydrolysed by boiling with hydrochloric acid to methylaniline and *isoethionic acid*. *Vinylsulphonbenzanilide*,  $\text{CH}_2\text{:CH}\cdot\text{SO}_2\cdot\text{NPh}\cdot\text{C}_6\text{H}_5$ , crystallises from dilute alcohol in slender prisms melting at 87°; *vinylsulphonacetanilide*,



separates from the same solvent in slender needles and melts at 100°.

*Propylenesulphanilide*,  $\text{CHMe}\cdot\text{CH}\cdot\text{SO}_2\cdot\text{NHPh}$ , prepared from propylenedisulphonic chloride, crystallises from alcohol in needles or leaflets and melts at 91°; the corresponding methylanilide is similar and melts at 58°.

*Trimethylenedisulphonanilide*,  $\text{CH}_2(\text{CH}_2\cdot\text{SO}_2\cdot\text{NHPh})_2$ , obtained by warming trimethylenedisulphonic chloride with aniline dissolved in benzene, crystallises from alcohol in lustrous leaflets and melts at 130°; it is not hydrolysed by hot dilute acids or alkalis and yields an amorphous *silver salt*,  $\text{C}_{15}\text{H}_{16}\text{O}_4\text{N}_2\text{S}_2\text{Ag}_2$ , which is decomposed by warm water.

*Trimethylenedisulphonbenzanilide*,  $\text{CH}_2(\text{CH}_2\cdot\text{SO}_2\cdot\text{NPh}\cdot\text{C}_6\text{H}_5)_2$ , forms slender, colourless needles melting at 160°; *trimethylenedisulphonacetanilide* is similar and melts at 176°.

*Ethylsulphanilide*,  $\text{C}_2\text{H}_5\cdot\text{SO}_2\cdot\text{NHPh}$ , obtained from ethylsulphonic chloride and aniline, forms colourless needles and melts at 55°; the *benzylanilide* crystallises in lustrous leaflets and melts at 100°, and the *acetylanilide* in rhombic plates melting at 110°.

All the foregoing anilides have a strongly acid character, being soluble in dilute aqueous alkalis. It should be noted that in their formation sulphur dioxide is eliminated only in the case of the  $\alpha\beta$ - and not in that of  $\alpha\gamma$ -disulphonic chlorides; the former yield monosulphanilides, the latter disulphanilides. W. A. D.

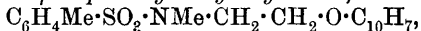
**Compounds of the Ethylenimine Series.** By WILHELM MARCKWALD and O. FROBENIUS (*Ber.*, 1901, **34**, 3544—3558).—*p-Toluenesulphonmethylbromomethylamide*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ , prepared by heating dry sodium toluenesulphonmethylamide with ethylene bromide, separates from carbon disulphide in white crystals, melts at



76·5°, and is readily soluble in most solvents; when heated with strong hydrobromic acid at 160°, it is decomposed into toluene, sulphuric acid, and methylbromoethylamine.

*Methylbromoethylamine*,  $\text{NHMe} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Br}$ , yields a *platinichloride* which forms dark red crystals, dissolves readily in water, and melts at 202—203°; the *picrate* forms orange crystals, dissolves in hot water, and melts at 114°.

*p-Toluenesulphon-β-naphthoxymethylethylamide*,



forms white crystals, dissolves readily in boiling alcohol and melts at 109·5°. *Methylchloroethylamine*,  $\text{NHMe} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Cl}$ , prepared by heating the preceding compound with hydrochloric acid at 170°, yields a *hydrochloride* which crystallises from hot acetone in white, hygroscopic crystals and melts at 108—112°; the *platinichloride* crystallises from hot alcohol and melts at 219°; the *picrate* forms yellow crystals and melts at 105°; when heated with water and a little hydrogen chloride, the base gives Knorr and Matthes' methylethanolamine,  $\text{NHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$  (Abstr., 1898, i, 399); with sodium sulphocyanide, it gives methyliminothiazolidine,  $\begin{array}{c} \text{CH}_2 - \text{S} \\ | \quad \quad \quad \diagup \\ \text{CH}_2 \cdot \text{NMe} \quad \text{C:NH} \end{array}$ .

*Methylchloroethylbenzamide*,  $\text{NMeBz} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Cl}$ , when boiled with water, is converted into *benzoylethanolmethylamine*,  $\text{NHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OBz}$ , an oily base, the *hydrochloride* of which crystallises from acetone in white, glistening flakes, dissolves readily in water, and melts at 143°; the corresponding *platinichloride* forms a golden-yellow powder and melts at 195°; the *picrate* forms yellow crystals and melts at 155°; the constitution of this base was proved by hydrolysis to benzoic acid and methylethanolamine.

*Benzoylethanolnitrosomethylamine*,  $\text{NO} \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OBz}$ , is a yellow oil.

*N-Methylethylenimine*,  $\begin{array}{c} \text{CH}_2 \\ | \quad \quad \diagup \\ \text{CH}_2 \quad \text{NMe} \end{array}$ , prepared by the action of alkalis on

chloroethylamine, boils at 27·5° under 764 mm. pressure; it is a mobile liquid which fumes in the air, is miscible with water, has a sp. gr. 0·7572 at 19·5°, coefficient of refraction 0·3885 at 19°,  $M_D = 17·78$ ; the *picrate* forms yellow crystals and melts at 120—122°; the *aurichloride* is a yellow, crystalline precipitate and melts at 95°; the base is stable towards permanganate and bromine water, but is converted by hydrochloric acid to chloroethylmethylamine, by sulphur dioxide to methyltaurine, by dilute sulphuric acid to methylethanolamine, and by methyl iodide to trimethyliodoethylammonium iodide,  $\text{CH}_2\text{I} \cdot \text{CH}_2 \cdot \text{NMe}_3\text{I}$ , but is indifferent towards carbon disulphide and ethyl oxalate.

*Benzenesulphonmethylchloroethylamide*,  $\text{C}_6\text{H}_5 \cdot \text{SO}_2 \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Cl}$ , prepared by the action of benzoyl chloride on the base, crystallises from light petroleum in white needles melting at 65—66°; similarly with benzoyl chloride, it yields methylchloroethylbenzamide.

A *polymeric* base,  $\text{C}_6\text{H}_{14}\text{N}_2$ , is also formed by the action of alkalis on methylchloroethylamine; it boils at 128—130° and is dibasic; the *picrate*,  $\text{C}_6\text{H}_{14}\text{N}_2(\text{C}_6\text{H}_5\text{O}_7\text{N}_3)_2$ , forms a yellow, crystalline precipitate and decomposes at 260° without melting; the *platinichloride* is an orange

coloured, crystalline precipitate and melts and decomposes at  $163^{\circ}$ ; the base is stable towards acids, reduces alkaline permanganate, is not identical with N-dimethylpiperazine, yields a soluble *ferrocyanide* which forms a white, soluble powder, and is therefore probably a tertiary base.

1- $\beta$ -Naphthoxyethylpiperidine,  $C_8NH_{10} \cdot CH_2 \cdot CH_2 \cdot OC_{10}H_7$ , crystallises from light petroleum in white needles and melts at  $47-49^{\circ}$ ; the *hydrochloride* forms white crystals, and the *platinichloride* large crystals, which soften at  $90^{\circ}$ , and melt and decompose at  $100-110^{\circ}$ ; the *picrate* crystallises from alcohol and melts at  $160-161^{\circ}$ ; the *dichromate* is insoluble in water or alcohol. 1-Chloroethylpiperidine,  $C_5NH_{10} \cdot CH_2 \cdot CH_2Cl$ , prepared by heating the preceding base with hydrochloric acid at  $150^{\circ}$ , is a yellow oil, moderately soluble in water; the *hydrochloride* separates from acetone in white crystals and becomes brown and melts at  $208^{\circ}$ ; the yellow *aurichloride* is readily soluble in hot water and in alcohol and melts at  $119-120^{\circ}$ ; the *picrate* crystallises from alcohol and melts at  $116-117^{\circ}$ . When heated with dilute sulphuric acid, the base is converted into Ladenburg's 1- $\beta$ -hydroxyethylpiperidine (Abstr., 1882, 165). When heated, the chloroethylpiperidine is converted by isomeric

change into *ethylenepiperidinium chloride*,  $CH_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} NCl \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}$ ,

which separates from alcohol in white crystals; aqueous alkalis do not precipitate a base, but when the chloride is acted on by silver oxide, an alkaline solution is obtained which leaves a syrupy, quaternary base on evaporation; the *platinichloride* is an orange-coloured, insoluble precipitate; the *aurichloride* forms yellow, insoluble crystals and melts and decomposes at  $273-274^{\circ}$ ; when heated on a water-bath with concentrated hydrochloric acid for an hour, the base is reconverted into chloroethylpiperidine hydrochloride.

The study of the two polymethylenimine bases here described has completely confirmed Howard and Marckwald's view (Abstr., 1900, i, 749) that Gabriel's 'vinylamine' is a ring-compound, as represented

by the formula  $\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix} > NH$ .

T. M. L.

**Bromoallylamine.** By H. RUDZICK (*Ber.*, 1901, 34, 3543).—In order to ascertain whether the two bases described by Paal (Abstr., 1889, 117) were ethylene or polymethylenimine derivatives, bromoallylamine was treated with toluenesulphonic chloride. *Toluene p-sulphobromoallylamine*,  $C_6H_4Me \cdot SO_3 \cdot NH \cdot C_3H_4Br$ , crystallises from light petroleum and melts at  $45-46^{\circ}$ ; it dissolves completely in alkalis, showing that the base is a primary amine, as suggested by Paal, and not a ring-compound.

T. M. L.

**Action of Ammonia on Benzyl Chloride, and the Conditions of Formation of Benzylamine.** By RENÉ DHOMMÉE (*Compt. rend.*, 1901, 133, 636—638. Compare Mason, *Trans.*, 1893, 63, 1313).—The author has investigated the conditions under which benzyl chloride and ammonia give the best yield of benzylamine. The reaction takes place most rapidly in the presence of ethyl alcohol, and

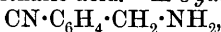
is retarded by the use of higher alcohols (amyl) as solvent. When a large excess of a saturated solution of ammonia in 60 per cent. alcohol at a temperature of 15° was employed, 44·5 per cent. of the benzyl chloride was converted into benzylamine, only a small quantity of dibenzylamine and no tribenzylamine being formed at the same time.

K. J. P. O.

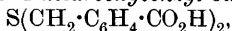
*m*-Cyanobenzyl Chloride. By FELIX EHRLICH (*Ber.*, 1901, 34, 3366—3377).—*m*-Cyanobenzylphthalimide is converted by alcoholic potash into *m*-cyanobenzylphthalamic acid,



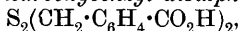
which crystallises in small, silky needles and melts at 175°, losing water and reforming the phthalimide. When the aqueous solution of the acid is evaporated, a portion of the substance is reconverted into the phthalimide, whilst the remainder is hydrolysed with formation of cyanobenzylamine and phthalic acid. *m*-Cyanobenzylamine,



is a brownish coloured oil, which is miscible with water and unites with the carbon dioxide of the atmosphere. The *hydrochloride* melts at 221—222°; the *picrate*,  $\text{C}_8\text{H}_3\text{N}_2\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3\cdot\frac{1}{2}\text{H}_2\text{O}$ , melts and decomposes at 217°; the *platinichloride* melts at 240° and the *oxalate* melts and decomposes at 196·5°. *Di-m*-cyanobenzylamine,  $\text{NH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN})_2$ , is formed by the action of alcoholic ammonia on cyanobenzyl chloride and crystallises in matted needles which are sparingly soluble in water and melt at 54°. The *hydrochloride* melts at 234—235°; the *platinichloride* melts and decomposes at 231°; the *aurichloride* melts at 209°, the *picrate* melts at 170°, and the *dichromate* decomposes at above 250°. *Tri-m*-cyanobenzylamine,  $\text{N}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN})_3$ , is formed together with the foregoing compound and by the action of cyanobenzyl chloride on dicyanobenzylamine, and crystallises in rhombic tablets melting at 118—119°. The *hydrochloride* is decomposed by water. The base is converted by hydrochloric acid at 120—130° into *tribenzylamine-m-tricarboxylic acid*,  $\text{N}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_3$ , which crystallises in microscopic needles and melts and decomposes at 248—249°. *m*-Cyanobenzyl thiocyanate is obtained by the action of the chloride on potassium thiocyanate and crystallises in plates, tablets, or small prisms melting at 55°. On hydrolysis with hydrochloric acid at the atmospheric pressure, it yields *m*-dicarboxybenzyl sulphide,



crystallising in fascicular groups of silky needles which melt at 197°; the *silver* salt is a white precipitate. Hydrochloric acid at 170° converts the thiocyanate into *m*-dicarboxybenzyl disulphide,

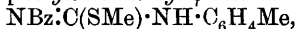


which crystallises in needles melting at 200—202° and can also be prepared from *m*-cyanobenzyl disulphide by hydrolysis. The thiocyanate is converted by the action of hydrogen sulphide into *m*-cyanobenzyl disulphide,  $\text{S}_2(\text{C}_7\text{H}_6\cdot\text{CN})_2$ , which forms radiating groups of needles and melts at 116—117°. *m*-Cyanobenzyl sulphide,  $\text{S}(\text{C}_7\text{H}_6\cdot\text{CN})_2$ , obtained by the action of potassium sulphide on cyanobenzyl chloride, crystallises in stellate and fan-shaped groups of prisms, melting at 99·5°. Nitric acid converts it almost quantitatively into isophthalic

acid. *m*-Cyanobenzyl mercaptan,  $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{SH}$ , is prepared by the action of the chloride on potassium hydrogen sulphide, and crystallises in spherical masses melting at  $24-25^\circ$ ; oxidation converts it into the disulphide. *p*-Nitro-*m*-cyanobenzyl chloride,  $\text{CN}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{CH}_2\text{Cl}$ , is obtained by the action of nitric acid on the chloride and crystallises in brownish-yellow plates melting at  $59-60^\circ$ . The anilide melts at  $135^\circ$ . On reduction, it is converted into *p*-amino-*m*-toluonitrile,  $\text{CN}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}_2$  [ $\text{Me}:\text{CN}:\text{NH}_2 = 1:3:4$ ], which crystallises in lustrous needles or plates melting at  $60-61^\circ$ , and is converted by hydrochloric acid at  $100^\circ$  into 4-amino-*m*-toluic acid melting at  $172.5^\circ$ . The hydrochloride of this amino-acid melts at  $200-201^\circ$ , whilst it is stated by Panaotovic (*J. pr. Chem.*, 1886, [ii], 33, 62) to melt at  $207^\circ$ . When heated with formamide, the acid yields 4-hydroxy-6-methylquinazoline,  $\text{C}_6\text{H}_3\text{Me}\cdot\text{C}(\text{OH})\cdot\text{N}=\text{N}-\text{CH}$ , melting at  $251^\circ$  and forming a platini-chloride which melts and decomposes at about  $290^\circ$ . This reaction proves that the aminotoluic acid actually has the constitution assigned to it above. *p*-Cyanobenzylphthalamic acid crystallises in nacreous plates and melts and decomposes at  $192^\circ$ . *p*-Cyanobenzylamine is a basic oil; the hydrochloride melts at  $274^\circ$ ; the picrate melts at  $218^\circ$ , and the platinichloride melts and decomposes at  $250^\circ$ . A. H.

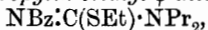
Some Acetyl- and Benzoyl- $\psi$ -thiocarbamides. By HENRY L. WHEELER and TREAT B. JOHNSON (*Amer. Chem. J.*, 1901, 26, 408-418).—The acyliminodithiocarbonic esters (Abstr., 1901, i, 705) react with amines at the ordinary temperature with formation of acyl- $\psi$ -thiocarbamides, thus:  $\text{NBz}\cdot\text{C}(\text{SMe})_2 + \text{NHR}' = \text{NBz}\cdot\text{C}(\text{SMe})\cdot\text{NRR}' + \text{MeHS}$ . The acyl- $\psi$ -thiocarbamides have no basic properties; those which contain a NH group are soluble in alkali; those derived from primary amines are decomposed by heat with formation of mercaptan, substituted acid amides, and other products, whilst those derived from secondary amines can be distilled under reduced pressure without decomposition. When treated with hydrochloric acid, they undergo hydrolysis in the following manner:  $\text{NBz}\cdot\text{C}(\text{SEt})\cdot\text{NHPh} + \text{H}_2\text{O} = \text{NHBz}\cdot\text{CO}\cdot\text{SEt} + \text{C}_6\text{H}_5\cdot\text{NH}_2$ . By the action of alcoholic ammonia, guanidine derivatives are formed. They readily react with phenylhydrazine with production of aminotriazoles.

When dimethyl acetyliminodithiocarbonate is treated with alcoholic ammonia, guanidine is produced. *Acetyldiisobutylthiolmethyl- $\psi$ -thiocarbamide*,  $\text{NAc}\cdot\text{C}(\text{SMe})\cdot\text{N}(\text{C}_4\text{H}_9)_2$ , is a yellow oil which boils at  $175-177^\circ$  under 22 mm. pressure. *Acetylphenylthiolmethyl- $\psi$ -thiocarbamide*,  $\text{NAc}\cdot\text{C}(\text{SMe})\cdot\text{NHPh}$ , forms long, colourless needles and melts at  $82-83^\circ$ . *Benzoyl-p-tolylthiolmethyl- $\psi$ -thiocarbamide*,

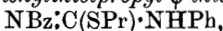


crystallises in prisms and melts at  $130^\circ$ . *Benzoyl- $\alpha$ -naphthylthiolmethyl- $\psi$ -thiocarbamide*,  $\text{NBz}\cdot\text{C}(\text{SMe})\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$ , crystallises in slender needles and melts at  $124^\circ$ . *Benzoyl-m-nitrophenylthiolmethyl- $\psi$ -thiocarbamide*,  $\text{NBz}\cdot\text{C}(\text{SMe})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , crystallises in prisms and melts at  $71-72^\circ$ . *Acetyldiethylthioethyl- $\psi$ -thiocarbamide*,  $\text{NAc}\cdot\text{C}(\text{SEt})\cdot\text{NEt}_2$ , is a yellow oil which distils at  $162-164^\circ$  under 21 mm. pressure. *Acetylphenylmethylthioethyl- $\psi$ -thiocarbamide*,  $\text{NBz}\cdot\text{C}(\text{SEt})\cdot\text{NMePh}$ , crys-

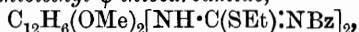
tallises in prisms and melts at  $66^{\circ}$ . *Benzoyldiethylthioethyl- $\psi$ -thiocarbamide*,  $\text{NBz}\cdot\text{C}(\text{SEt})\cdot\text{NEt}_2$ , forms colourless, rectangular prisms and melts at  $70^{\circ}$ . *Benzoyldipropylthioethyl- $\psi$ -thiocarbamide*,



is a yellow oil which boils at  $226\text{--}229^{\circ}$  under 17 mm. pressure. *Benzoyldiisobutylthioethyl- $\psi$ -thiocarbamide*,  $\text{NBz}\cdot\text{C}(\text{SEt})\cdot\text{N}(\text{C}_4\text{H}_9)_2$ , boils at  $234\text{--}236^{\circ}$  under 21 mm. pressure. *Benzoyl-p-tolylthioethyl- $\psi$ -thiocarbamide*,  $\text{NBz}\cdot\text{C}(\text{SEt})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , crystallises in prisms and melts at  $93^{\circ}$ ; it reacts with phenylhydrazine with formation of mercaptan and diphenyl-p-tolylaminotriazole, which crystallises in stout prisms and melts at  $225\text{--}226^{\circ}$ . *Benzoyl- $\psi$ -cumylthioethyl- $\psi$ -thiocarbamide*,  $\text{NBz}\cdot\text{C}(\text{SEt})\cdot\text{NH}\cdot\text{C}_6\text{H}_2\text{Me}_3$ , forms slender needles and melts at  $83\text{--}84^{\circ}$ . *Benzoyl-p-anisylthioethyl- $\psi$ -thiocarbamide*,  $\text{NBz}\cdot\text{C}(\text{SEt})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , crystallises in slender prisms and melts at  $99\text{--}100^{\circ}$ . *Benzoyldiphenylthioethyl- $\psi$ -thiocarbamide*,  $\text{NBz}\cdot\text{C}(\text{SEt})\cdot\text{NPh}_2$ , crystallises in prisms and melts at  $142^{\circ}$ . *Benzoylphenylthiolpropyl- $\psi$ -thiocarbamide*,



crystallises in prisms and melts at  $78\text{--}79^{\circ}$ . *Benzoyl-p-tolylthiolpropyl- $\psi$ -thiocarbamide*,  $\text{NBz}\cdot\text{C}(\text{SPr})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , crystallises in needles and melts at  $81\text{--}81.5^{\circ}$ . *Benzoyl-m-chlorophenylthiolpropyl- $\psi$ -thiocarbamide*,  $\text{NBz}\cdot\text{C}(\text{SPr})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$ , forms colourless prisms and melts at  $59\text{--}59.5^{\circ}$ . *Benzoylphenyleneguanidine*,  $\text{NBz}\cdot\text{C}(\text{NH})_2\cdot\text{C}_6\text{H}_4$ , obtained by the action of o-phenylenediamine on diethylbenzoyliminodithiocarbonate, crystallises in minute prisms and melts at  $237^{\circ}$ . *Diphenylenebisbenzoylthioethyl- $\psi$ -thiocarbamide*,  $\text{C}_{12}\text{H}_8[\text{NH}\cdot\text{C}(\text{SEt})\cdot\text{NBz}]_2$ , crystallises in needles and melts and decomposes at  $179^{\circ}$ ; it reacts with phenylhydrazine to form the *bistriazole*,  $\text{C}_{12}\text{H}_8(\text{NH}\cdot\text{C}_2\text{N}_3\text{Ph}_2)_2$ , which crystallises from alcohol and does not melt below  $265^{\circ}$ . *Dimethoxydiphenylenebisbenzoylthioethyl- $\psi$ -thiocarbamide*,

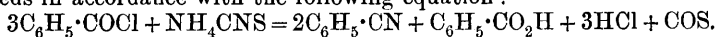


crystallises in minute, colourless needles and melts at  $170\text{--}171^{\circ}$ . *Benzoylphenylthiolbenzyl- $\psi$ -thiocarbamide*,  $\text{NBz}\cdot\text{C}(\text{S}\cdot\text{C}_6\text{H}_5)\cdot\text{NHPh}$ , may be prepared by the action of aniline on benzyl benzoyliminodithiocarbonate, by the action of benzoic anhydride on phenylbenzyl- $\psi$ -thiocarbamide, or by the action of benzyl chloride on benzoylphenylthiocarbamide in presence of sodium hydroxide or sodium ethoxide; it crystallises in small prisms and melts at  $116\text{--}117^{\circ}$ . When this compound is warmed with hydrochloric acid, *thiobenzylbenzoylcarbamate*,  $\text{NH}\cdot\text{Bz}\cdot\text{CO}\cdot\text{S}\cdot\text{C}_6\text{H}_5$ , is produced, which crystallises in needles and melts at  $141\text{--}142^{\circ}$ . *Benzoylphenylguanidine*,  $\text{NBz}\cdot\text{C}(\text{NH}_2)\cdot\text{NHPh}$ , obtained by the action of alcoholic ammonia on benzoylphenylthiolbenzyl- or benzoylphenylthioethyl- $\psi$ -thiocarbamide, crystallises in minute, light yellow prisms and melts at  $90\text{--}91^{\circ}$ ; the *picrate* melts at  $186^{\circ}$ . *Benzoylphenylthiol-m-xyl- $\psi$ -thiocarbamide*,  $\text{NBz}\cdot\text{C}(\text{S}\cdot\text{C}_8\text{H}_9)\cdot\text{NHPh}$ , crystallises in prisms and melts at  $110\text{--}111^{\circ}$ . *Benzoyl- $\alpha$ -naphthylthiol-m-xyl- $\psi$ -thiocarbamide*,  $\text{NBz}\cdot\text{C}(\text{S}\cdot\text{C}_{10}\text{H}_7)\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$ , forms colourless, flattened prisms and melts at  $133^{\circ}$ .

E. G.

**Action of Benzoyl Chloride on Ammonium Thiocyanate.**  
By GIDEON BENSON and HOMER W. HILLYER (*Amer. Chem. J.*, 1901, 26, 373—377).—When ammonium thiocyanate (1 mol.) is heated with

benzoyl chloride (3 mols.), hydrogen chloride, carbon dioxide, and carbon oxysulphide are evolved, and benzoic acid and benzonitrile are produced. Estimation of the products shows that the reaction proceeds in accordance with the following equation :



E. G.

**Thiocyanates and isoThiocyanates.** [Thiocarbimides]. By HENRY L. WHEELER [and, in part, TREAT B. JOHNSON] (*Amer. Chem. J.*, 1901, 26, 345—360).—*Diethyl thiocyanomalonate*,  $\text{NCS}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , obtained by warming diethyl chloromalonate with potassium thiocyanate, is a colourless oil which boils at  $169\text{--}170^\circ$  under  $22\text{--}23$  mm. pressure; by the action of strong hydrochloric acid, it is converted into 3:5-diketotetrahydrothiazole. When diethyl thiocyanomalonate is heated with thiobenzoic acid, the *diethyl malonate* derivative of *benzoyldithiocarbamic acid*,  $\text{NHBz}\cdot\text{CS}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , is produced, which forms long, yellow, flattened prisms or plates and melts at  $119^\circ$ .

When tricarbethoxychloromethane is boiled with alcoholic potassium thiocyanate, no reaction takes place.

Ethyl phenylchloroacetate boils at  $142\text{--}145^\circ$  under  $17\text{--}18$  mm. pressure, and when warmed with alcoholic ammonium thiocyanate yields *ethyl phenylthiocyanoacetate*,  $\text{NCS}\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$ , which boils at  $182\text{--}184^\circ$  under  $17$  mm. pressure; this substance is converted by concentrated hydrochloric acid into 2-phenyl-3:5-diketotetrahydrothiazole,

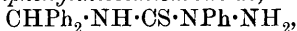
$\text{NH}\begin{smallmatrix} \text{CO}\cdot\text{S} \\ | \\ \text{CO}\cdot\text{CHPh} \end{smallmatrix}$ , which crystallises in colourless prisms, melts at  $125\text{--}126^\circ$ , and dissolves readily in alcohol and sparingly in water.

By the action of aniline on ethyl phenylthiocyanoacetate, *diphenyl-ψ-thiohydantoin*,  $\text{NPh}\begin{smallmatrix} \text{C}(\text{NH})\cdot\text{S} \\ | \\ \text{CO}\text{---}\text{CHPh} \end{smallmatrix}$ , is obtained, which crystallises

in needles or plates and melts at  $185\text{--}186^\circ$ . When ethyl phenylthiocyanoacetate is heated with thiobenzoic acid, the *ethyl phenylacetate* derivative of *benzoyldithiocarbamic acid*,  $\text{NHBz}\cdot\text{CS}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$ , is produced, which crystallises in thin, yellow plates and melts at  $150\text{--}154^\circ$ .

*Diphenylmethylthiocarbimide*,  $\text{CHPh}_2\cdot\text{NCS}$ , obtained by heating diphenylmethyl bromide with ammonium or potassium thiocyanate, distils at  $222\text{--}225^\circ$  under  $37\text{--}38$  mm. pressure as a blue liquid which solidifies on cooling; it crystallises from alcohol in colourless prisms and melts at  $61^\circ$ . *Diphenylmethylacetamide*,  $\text{CH}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{CHPh}_2$ , formed by the action of thioacetic acid on the thiocarbimide, crystallises in colourless needles, melts at  $146\text{--}147^\circ$ , and is readily hydrolysed by strong hydrochloric acid with production of benzhydramine hydrochloride. The corresponding *benzamide*,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NH}\cdot\text{CHPh}_2$ , crystallises in silky needles and melts at  $166\text{--}167^\circ$ . *Diphenylmethylthiocarbamide*,  $\text{CHPh}_2\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$ , obtained by the action of ammonia on the thiocarbimide, forms long, silky needles and melts at  $189^\circ$ . *Diphenylmethylmethylthiocarbamide*,  $\text{CHPh}_2\cdot\text{NH}\cdot\text{CS}\cdot\text{NHMe}$ , crystallises in colourless, flattened prisms and melts at  $152^\circ$ . *Diphenylmethyldiethylthiocarbamide*,  $\text{CHPh}_2\cdot\text{NH}\cdot\text{CS}\cdot\text{NEt}_2$ , crystallises in colourless needles and melts at  $112\text{--}113^\circ$ ; *diphenylmethyldiisobutylthiocarbamide* forms

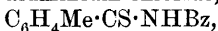
long, colourless needles and melts at 97—98°. Diphenylmethylphenylthiocarbamide melts at 178°. *Diphenylmethylphenylmethylthiocarbamide*,  $\text{CHPh}_2 \cdot \text{NH} \cdot \text{CS} \cdot \text{NPhMe}$ , crystallises in long, slender needles and melts at 119—120°; *diphenylmethyl-β-naphthylthiocarbamide*,  $\text{CHPh}_2 \cdot \text{NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7$ , forms colourless needles and melts at 179°. *Diphenylmethylphenylthiosemicarbazide*,



crystallises in colourless plates and melts at 178°; if the temperature is maintained at 178°, or a little higher, for a few seconds, the substance solidifies, and then melts and decomposes at 198°.

When triphenylmethyl thiocyanate is heated with thioacetic acid, *triphenylmethyl thiolacetate*,  $\text{CH}_3 \cdot \text{CO} \cdot \text{S} \cdot \text{CPh}_3$ , is obtained, which crystallises in colourless prisms and melts at 138—140°. The corresponding *thiolbenzoate* forms colourless prisms and melts at 184—185°. If a solution of triphenylmethyl thiocyanate in benzene is mixed with alcoholic ammonia, left for three days, and then evaporated to dryness, a residue is obtained, part of which is soluble in water and the remainder in benzene; the aqueous solution contains triphenylmethylcarbinol and ammonium thiocyanate, whilst the benzene solution, after treatment with dry hydrogen chloride, yields triphenylmethylamine hydrochloride and triphenylmethyl ethyl ether. By the action of aniline on triphenylmethyl thiocyanate, phenylthiocarbamide is produced. Phenylhydrazine reacts with the thiocyanate with formation of phenylthiosemicarbazide and the unstable triphenylmethanehydrazobenzene described by Gomberg (Abstr., 1897, i, 623). From these experiments, the author concludes that the triphenylmethyl thiocyanate is a normal thiocyanate.

Benzoylthiocarbimide reacts with ethyl sodiomalonate, sodium formanilide, sodium phenoxide, or ethyl acetoacetate, and in each case sodium thiocyanate is produced. By the action of benzoylthiocarbimide on toluene in presence of aluminium chloride, a *compound*,

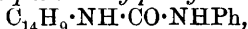


is obtained, which crystallises from alcohol in red prisms and melts at 135—136°. With phenetole under similar conditions, *p*-ethoxythiobenzamide, melting at 158°, is produced.

Benzoylthiocarbimide combines with hydrogen phosphide to form the *phosphocarbamide*,  $\text{NHBz} \cdot \text{CS} \cdot \text{PH}_3$ , as an orange precipitate, which melts at 155—157° and is readily soluble in alcohol but only sparingly so in benzene.

E. G.

**3-Nitro- and 3-Amino-phenanthrene.** By JULIUS SCHMIDT (*Ber.*, 1901, 34, 3531—3535).—3-Nitrophenanthrene has been described by G. A. Schmidt (Abstr., 1879, i, 941) as  $\gamma$ -nitrophenanthrene and is reduced to 3-aminophenanthrene (Werner and Kunz, Abstr., 1901, i, 696, and G. A. Schmidt, *loc. cit.*); the *benzoyl* derivative of the base crystallises from alcohol in white, felted needles and melts at 213—214°; 3-phenanthrylurethane,  $\text{C}_{14}\text{H}_9 \cdot \text{NH} \cdot \text{CO}_2\text{Et}$ , crystallises from dilute alcohol in glistening, pale-yellow flakes and melts at 120—121°; *s*-3-phenanthrylphenylcarbamide,



does not melt at  $300^{\circ}$ ; when diazotised, the base is converted into 3-hydroxyphenanthrene (Pschorr, Abstr., 1900, i, 488). T. M. L.

**Nitro-compounds of Anthragallol. II.** By MAX BAMBERGER and FRITZ BÖCK (*Monatsh.*, 1901, 22, 717—731. Compare Abstr., 1897, i, 576).— $\psi$ -Nitroanthragallol is best prepared by the action of the dry vapour of nitric acid (from nitric and sulphuric acids) on anthragallol (compare *loc. cit.*).  $\alpha$ -Nitroanthragallol is purified by crystallisation from a mixture of alcohol and benzene, from which it separates in dark ruby-red prisms containing 1 mol. of benzene; it forms a *triacetyl* derivative,  $\text{NO}_2 \cdot \text{C}_{14}\text{H}_4\text{O}_5\text{Ac}_3$ , which crystallises in lemon-yellow needles melting at  $233^{\circ}$ .

Concentrated aqueous hydrochloric acid converts  $\psi$ -nitroanthragallol mainly into  $\beta$ -nitroanthragallol; but some chloronitroanthragallol is always simultaneously produced. In the presence of absolute alcohol and hydrogen chloride,  $\psi$ -nitroanthragallol yields monochloroanthragallol (Slama, Abstr., 1900, i, 181).  $\alpha$ -Nitroanthragallol is formed from  $\psi$ -nitroanthragallol by the action of anhydrous formic acid.

$\psi$ -Nitroanthragallol dissolves in pyridine, forming a steel-blue solution, which on heating becomes at first green and then reddish-brown. This solution contains the *pyridine* salt,  $\text{C}_{14}\text{H}_8\text{O}_5 \cdot \text{HNO}_3 \cdot \text{C}_5\text{NH}_5$ , which is obtained in indigo-blue crystals when acetone solutions of pyridine and  $\psi$ -nitroanthragallol are mixed. From acetyl chloride and  $\psi$ -nitroanthragallol is obtained a compound,  $\text{C}_{16}\text{H}_{10}\text{O}_8\text{NCl}(\text{?})$ , in red crystals, which decomposes at  $110^{\circ}$  with evolution of acetyl chloride.

The view is expressed that  $\psi$ -nitroanthragallol is an additive product of nitric acid and anthragallol, whilst  $\alpha$ - and  $\beta$ -nitroanthragallol are formed from it by the elimination of water. K. J. P. O.

**Nitro-compounds of Anthragallol. III.** By MAX BAMBERGER and FRITZ BÖCK (*Monatsh.*, 1901, 22, 732—736. Compare preceding abstract).—The authors have attempted to prepare compounds analogous to  $\psi$ -nitroanthragallol, from anthragallol derivatives, in which the hydroxyl groups are wholly or partly replaced.

Anthragallolamine,  $\text{C}_{14}\text{H}_5\text{O}_2(\text{OH})_2 \cdot \text{NH}_2$ , yields with concentrated nitric acid a derivative crystallising in orange-yellow needles, which explode at  $180^{\circ}$ ; it appears not to belong to the pseudo-series. Tribenzoylanthragallol, on nitration with vapour of nitric acid, did not yield a  $\psi$ -nitro-derivative; triacetylanthragallol, on the other hand, yielded such a compound.

The *dimethyl ether* of anthragallol,  $\text{OH} \cdot \text{C}_{14}\text{H}_5\text{O}_2(\text{OMe})_2$ , prepared from anthragallol and methyl sulphate, crystallises in yellowish-green needles melting at  $160^{\circ}$ , and is soluble in potassium hydroxide with a red colour. It does not appear to be identical with two dimethyl ethers previously described by Perkin and Hummel (*Trans.*, 1893, 63, 1168).

K. J. P. O.

**Some Esters of Cholesterol and Phytosterol.** By A. BÖMER and K. WINTER (*Zeit. Nahr.-Genussm.*, 1901, 4, 865—888).—The authors have prepared the formic, acetic, propionic, butyric, and benzoic esters of both cholesterol and phytosterol, the latter being obtained from



various oils, and melting at slightly different temperatures. Excepting the benzoate, which was prepared by heating the alcohols with benzoyl chloride in an open tube at  $160^{\circ}$ , the esters were obtained by heating the alcohols with five times their weight of the acids or their anhydrides in a sealed tube in the water-bath.

Full details are given of their chemical and crystallographical properties. The melting points of some of the esters of phytosterol, which differ with the source of the latter, are considerably higher than those of cholesterol, and in this way the two alcohols may be distinguished. The elementary composition of phytosterol whether prepared from cotton oil, ground nut oil, sesamé oil, colza oil, poppy oil, hempseed oil, linseed oil, or castor oil, is, however, the same; cholesterol has also the same composition (compare Abstr., 1899, ii, 191, 192, 259; 1900, ii, 178).

L. DE K.

**The Formation of Acid Chlorides by means of Thionyl Chloride.** By HANS MEYER (*Monatsh.*, 1901, 22, 777—802. Compare Abstr., 1901, i, 407, 628).—*p*-Chloro- and *p*-bromo-benzoic acids only yield acid chlorides after long boiling with thionyl chloride; *p*-iodobenzoic acid reacts with thionyl chloride more readily. *p*-Iodobenzamide, formed from the acid chloride and ammonia, is a crystalline powder melting at  $209^{\circ}$ . *o*-Nitro- and *o*-hydroxyterephthalic chlorides are easily obtained; 2-aldehydo-5:6-methoxybenzoyl chloride (opianic chloride) is immediately formed from the acid and thionyl chloride at the ordinary temperature, and crystallises in yellow needles melting and decomposing at  $83$ — $84^{\circ}$ . 8-Aldehydonaphthoic chloride is prepared with similar ease. The acid chloride obtained from benzoylbenzoic acid appears to be a mixture of the normal and pseudo-compounds, as with methyl alcohol it yields a mixture of two methyl esters. 1-Hydroxy-2-naphthoic chloride is a solid and with ammonia gives an amide which crystallises in needles melting at  $190^{\circ}$ . 2-Hydroxy-1-naphthoic and 3-hydroxy-2-naphthoic acids both yield chlorides; the compound from the latter acid is the more readily formed and crystallises in lemon-yellow needles melting at  $192^{\circ}$ ; with methyl alcohol, it gives a methyl ester in yellow needles, melting at  $72^{\circ}$ , and with ammonia an amide (m. p.  $188^{\circ}$ ). The groups OH and  $\text{CO}_2\text{H}$  in the para-position relatively to the  $\text{CO}_2\text{H}$  group hinder the formation of acid chlorides by thionyl chloride, whilst such groups as  $\text{NO}_2$  and Br favour the formation of these compounds.

Although phloroglucinolcarboxylic acid (2:4:6-trihydroxybenzoic acid) does not react with thionyl chloride, the trimethyl ether readily yields an acid chloride; the monomethyl ether described by Herzig and Wenzel (Abstr., 1901, i, 473) also gives an acid chloride and must therefore be 2:6-dihydroxy-4-methoxybenzoic acid.

Terephthalic acid does not, but  $\Delta^{1:4}$ -dihydroterephthalic acid does react with thionyl chloride, yielding a dichloride. Dibromoadipic,  $\alpha$ -dichloromuconic, and  $\Delta^{\beta\gamma}$ -dihydromuconic acids give dichlorides, whilst muconic acid does not react with thionyl chloride. Piperic chloride, prepared from piperic acid, crystallises in yellow needles melting at  $180^{\circ}$ , and the methyl ester prepared from it forms yellow leaflets melting at  $140^{\circ}$ .

K. J. P. O.

**The Three Cinnamic Acids.** By ARTHUR MICHAEL [and, in part, WILLIAM R. WHITEHORNE] (*Ber.*, 1901, **34**, 3640—3666. Compare Liebermann, *Abstr.*, 1890, 494, 620, and 1417; 1891, 832; 1892, 469 and 848; Erlenmeyer, *Abstr.*, 1886, 945; 1891, 200).—The author has prepared three isomeric cinnamic acids in a state of purity, namely, cinnamic acid, m. p. 133°; *allocinnamic* acid, m. p. 68°, and *isocinnamic* acid, m. p. 36—37°. It is thought probable that the fourth isomeride described by Erlenmeyer as melting at 38—46° is a mixture of the *allo*- and *iso*-acids.

When  $\beta$ -bromo*allocinnamic* acid, melting at 159°, is reduced with zinc dust and alcohol, the products are a minute quantity of cinnamic acid together with *allocinnamic* acid, 75 per cent., and *isocinnamic* acid, 25 per cent. The cinnamic acid is readily removed in the form of its calcium salt and the *allo*- and *iso*-acids may then be separated by crystallising their barium salts from methyl alcohol.

The following table of differences is given :

<i>iso</i> Cinnamic acid.	<i>allo</i> Cinnamic acid.
More readily soluble in most solvents.	—
Barium salt, with 2H <sub>2</sub> O, thin plates.	Barium salt, with 3H <sub>2</sub> O, feathery needles.
Soluble in 0.3 part of methyl alcohol or in 4 parts of acetone.	Soluble in 38 parts of methyl alcohol or in 124 parts of acetone.
Calcium salt, with 2H <sub>2</sub> O, soluble in 5 parts of acetone.	Calcium salt, with 3H <sub>2</sub> O, soluble in 50 parts of acetone.
Strontium salt, with 2H <sub>2</sub> O.	Strontium salt, with 3H <sub>2</sub> O.
Cadmium salt, anhydrous, soluble in 178 parts of water at 20°.	Cadmium salt, with 2H <sub>2</sub> O, soluble in 1010 parts of water at 20°.
Manganese salt, with 3H <sub>2</sub> O, soluble in cold water.	Manganese salt, with 2H <sub>2</sub> O; sparingly soluble even in hot water.

A small amount of the *iso*-acid is also obtained by the reduction of  $\alpha$ -bromo*allocinnamic* acid melting at 120°.  $\beta$ -Bromocinnamic acid (m. p. 134—135°),  $\beta$ -chloro*allocinnamic* acid (m. p. 142°),  $\beta$ -iodocinnamic acid (m. p. 128°), and  $\beta$ -iodo*allocinnamic* acid (m. p. 188°) all yield cinnamic acid and no trace of the *allo*- or *iso*-acid.

For the preparation of phenylpropionic acid, the authors recommend boiling  $\alpha$ -bromocinnamic acid with 20 per cent. alcoholic potassium hydroxide for 4 hours; when 2.5 mols. of alkali are used for each mol. of acid, the yield is 85 per cent. of the theoretical.

When phenylpropionic acid is left in contact with concentrated hydriodic acid for 24 hours at 0°, the product consists of a mixture of  $\beta$ -iodocinnamic acid melting at 127—129° and readily soluble in most organic solvents, and  $\beta$ -iodo*allocinnamic* acid, melting and decomposing at 186—188° and only sparingly soluble in cold organic solvents.

The addition of bromine to ethyl cinnamate has been studied under various conditions. In all cases, the product is a mixture of ethyl cinnamate dibromide melting at 74° and *ethyl cinnamate allodibromide* melting at 28—30°, the best yield of the latter, namely, 54 per cent., is obtained when an excess of bromine is employed in carbon tetrachloride solution in the dark and at 0°. The *allo*-compound forms large, prismatic crystals readily soluble in the ordinary organic solvents, and is regarded as the normal additive product, whereas the ester melting at 74° is regarded as formed by intramolecular rearrangement. Methyl cinnamate and bromine also yield a mixture of methyl cinnamate

dibromide melting at  $117^{\circ}$ , with an *allodibromide* melting at  $50-53^{\circ}$  which is identical with the product obtained by Liebermann (*loc. cit.*) by the union of methyl*allocinnamate* and bromine. The yield of *allo*-compound is greater when the combination occurs in the dark than in the light. The chief product obtained by the addition of bromine to cinnamic acid is the dibromide melting at  $201^{\circ}$  whilst only a small amount of *allodibromide* melting at  $91^{\circ}$  is formed.

*alloCinnamic acid*, when oxidised, yields the phenylglyceric acid melting at  $121^{\circ}$ . Ethyl cinnamate *allodibromide* and silver benzoate yield the dibenzoate melting at  $108-109^{\circ}$ , which is also obtained from the ethyl ester dibromide melting at  $74^{\circ}$  (*Ber.*, 1879, 12, 537).

The action of alcoholic sodium hydroxide on the two ethyl cinnamate dibromides has been studied. Three grams of *allodibromide* (m. p.  $28-30^{\circ}$ ) yield a mixture of 0.8 gram of  $\alpha$ -bromo*allocinnamic acid* melting at  $120^{\circ}$  and 1.2 grams of  $\alpha$ -bromocinnamic acid melting at  $131^{\circ}$ , whilst 3 grams of the isomeric ester yield 0.1 gram of the  $\alpha$ -bromo*allo*- and 1 gram of the  $\alpha$ -bromo-cinnamic acid.

The following salts of phenylpropionic (hydrocinnamic) acid are described. Barium salt, large plates soluble in 33 parts of water at  $27^{\circ}$  and in 1000 of methyl alcohol at  $25^{\circ}$ . Calcium salt, soluble in 23 parts of water at  $27^{\circ}$  and 30 parts of acetone at  $25^{\circ}$ . Nickel salt, pale green precipitate, soluble in hot water. The nickel, manganese, cobalt, and copper salts are all moderately soluble in cold water. J. J. S.

**Kolbe's Reaction for the Formation of Aromatic Hydroxy-carboxylic Acids in Indifferent Solvents and its Relation to the Cryoscopic Behaviour of the Phenols in Benzene and in other Hydroxyl-free Solvents.** By GIUSEPPE ODDO and E. MAMELI (*Gazzetta*, 1901, 31, ii, 244-254).—The formation of hydroxy-acids by the action of carbon dioxide on the corresponding phenoxides often gives better yields when an indifferent solvent, such as toluene, light petroleum, or alcohol, is present; this action is very marked in the cases of the carboxy-acids of the  $\alpha$ - and  $\beta$ -naphthols, and of phloroglucinol. The author finds that the more readily the hydroxy-acids are formed from phenols, the more readily do they decompose; salicylic acid, for example, is moderately stable, whilst the two naphthol-carboxylic acids and phloroglucinolmonocarboxylic acid readily decompose, even at the ordinary temperature. The less stable acids of the series react very readily with nitrous acid. From a study of the cryoscopic behaviour of: (1) *o*-cresol, which yields 5 per cent. of hydroxy-acid, in benzene and naphthalene; (2) *m*-xylenol, yielding 15 per cent. of hydroxy-acid, in benzene and naphthalene; (3) thymol, giving 50 per cent. of hydroxy-acid, in benzene and naphthalene; (4) carvacrol, which gives 15 per cent. of hydroxy-acid, in benzene; (5)  $\alpha$ - and  $\beta$ -naphthols, which yield almost theoretical quantities of the corresponding hydroxy-acids, in benzene; (6) creosol, yielding 10 per cent. of hydroxy-acid, in benzene, and (7) guaiacol, which gives no trace of the corresponding hydroxy-acid, in benzene, the authors conclude that no definite relation exists between the cryoscopic behaviour of phenols in hydroxyl-free solvents and their greater or less capacity for yielding hydroxy-acids by Kolbe's method. T. H. P.

**Condensation of Naphthalaldehydic Acid [8-Aldehydonaphthoic Acid] with Acetone and Acetophenone.** By JOSEF ZINK (*Monatsh.*, 1901, 22, 813—842).—8-Aldehydonaphthoic acid condenses with acetophenone in the presence of potassium hydroxide at 40—50° to yield *naphthalidomethyl phenyl ketone*,  $\text{COPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$ ,

or  $\begin{array}{c} \text{C}_{10}\text{H}_6\cdot\text{CH}\cdot\text{CH}_2\cdot\text{COPh} \\ \text{CO} \text{---} \text{O} \end{array}$ , which forms white needles melting at 127°.

With acetone, *naphthalidodimethyl ketone*,  $\text{C}_{15}\text{H}_{12}\text{O}_3$ , is formed, and crystallises in white leaflets melting at 76—78°. The *methyl ester* of *naphthalidomethyl phenyl ketone*,  $\text{C}_{21}\text{H}_{16}\text{O}_3$ , is prepared from the potassium salt and methyl iodide and crystallises in yellow needles melting at 90°. In acid solution, hydroxylamine and *naphthalidomethyl phenyl ketone* yield an *oxime*,  $\text{C}_{20}\text{H}_{15}\text{O}_3\text{N}$ , which crystallises in prisms melting at 123° and is decomposed into its components by hydrochloric acid. In alkaline solution, a *compound*,  $\text{C}_{20}\text{H}_{16}\text{O}_5\text{N}_2$ , is formed, which crystallises in needles melting at 165°, and is an *oxamino-oxime anhydride*,  $\text{N} \begin{array}{c} \text{CPh}\cdot\text{CH}_2 \\ \text{O} \text{---} \text{NH} \end{array} \text{CH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$ .

*Naphthalidodimethyl ketone* reacts with hydroxylamine both in alkaline and acid solution, forming *naphthalidodimethyl ketoxime*, the *hydrochloride*,  $\text{C}_{15}\text{H}_{14}\text{O}_3\text{NCl}$ , of which melts at 172—175°.

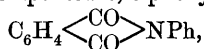
The *phenylhydrazone* of *naphthalidomethyl phenyl ketone*,  $\text{C}_{26}\text{H}_{20}\text{O}_2\text{N}_2$ , prepared from phenylhydrazine and the ketone, crystallises in needles melting at 155—160°, is insoluble in alkalis, and decomposed by hydrochloric acid into its components; by hydroxylamine hydrochloride it is converted into the *oxime*; the latter, with phenyl hydrazine, again yields the *hydrazone*. The *phenylhydrazone* of *naphthalidodimethyl ketone*,  $\text{C}_{21}\text{H}_{18}\text{O}_2\text{N}_2$ , crystallises in needles melting at 135—140°.

Ammonia converts *naphthalidomethyl phenyl ketone* into *phenacyl-naphthalimidine*,  $\text{CO} \begin{array}{c} \text{C}_{10}\text{H}_6 \\ \text{NH} \end{array} \text{CH}\cdot\text{CH}_2\cdot\text{COPh}$ , which crystallises in white needles melting at 163° and is converted by boiling hydrochloric acid and potassium hydroxide into an isomeric *compound*,  $\text{C}_{20}\text{H}_{16}\text{O}_2\text{N}$ , crystallising in lemon-yellow needles melting at 212°; as the latter is decomposed by prolonged boiling with potassium hydroxide with formation of acetophenone, it is represented by the formula  $\text{COPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}\cdot\text{NH}_2$ . The imidine yields, with hydroxylamine, an *oxime*,  $\text{C}_{20}\text{H}_{16}\text{O}_2\text{N}_2$ , which forms rhombohedral crystals melting at 208°.

In an analogous manner, *naphthalidodimethyl ketone* yields *acetonyl-naphthalimidine*,  $\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}$ , crystallising in white needles melting at 142°; this gives an *oxime*,  $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_2$ , crystallising in prisms and melting at 233°.

K. J. P. O.

**Action of Aromatic Amines on Phthalyl Chloride at different Temperatures.** By MITSURU KUHARA and M. FUKUI (*Amer. Chem. J.*, 1901, 26, 454—463).—When aniline reacts with phthalyl chloride at the ordinary temperature, *s*-phenylphthalimide,



melting at 203°, is produced; if, however, an ethereal solution of

phthalyl chloride, cooled to  $-10^{\circ}$ , is added to an ethereal solution of aniline at the same temperature,  $\alpha$ -phenylphthalimide,  $\text{C}_6\text{H}_4 > \text{C}:\text{NPh}$ ,  $\text{CO}\cdot\text{O}$ , is formed, which crystallises in groups of white, microscopic needles, melts at  $218^{\circ}$ , and is slightly soluble in alcohol and readily so in hot glacial acetic acid. When this compound is heated with *o*-xylene at  $140^{\circ}$  in a sealed tube, it is converted into the *s*-isomeride, whilst if it is heated with water under these conditions, *s*-phenylphthalimide, aniline, and phthalic acid are produced. It is decomposed by alcoholic ammonia with formation of aniline and ammonium phthalate, whilst, as Laurent and Gerhardt have shown (*Jahresb. Chem.*, 1847—1848, 605), the *s*-compound is thereby converted into ammonium phenylphthalamate. When *s*-phenylphthalimide is boiled with a solution of barium hydroxide, phenylphthamic acid is produced, but this substance is not formed when the  $\alpha$ -isomeride is similarly treated. By the action of nitrous acid on phenylphthamic acid, the *nitroso*-derivative,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NPh}\cdot\text{NO}$ , is obtained, which forms slender, pale yellow crystals, dissolves readily in water or alcohol, and is very unstable.

*o*-Tolylphthalimide,  $\text{C}_6\text{H}_4 > \text{C}:\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$ ,  $\text{CO}\cdot\text{O}$ , obtained in a manner similar to that by which  $\alpha$ -phenylphthalimide is prepared, crystallises in silky needles, melts at  $201^{\circ}$ , and is easily soluble in hot alcohol. When kept in a fused state for 3 hours, it is converted into the *s*-isomeride, and if heated with water at  $120^{\circ}$  for 7 hours in a sealed tube, phthalic acid, *o*-toluidine, and *s*-*o*-tolylphthalimide are produced. By the action of barium hydroxide, it is decomposed into *o*-toluidine and phthalic acid. The *nitroso*-derivative of *o*-tolylphthamic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{N}(\text{NO})\cdot\text{C}_6\text{H}_4\text{Me}$ , closely resembles the corresponding compound of phenylphthamic acid.

E. G.

**Pernitrososantonin and its Derivatives.** By LUIGI FRANCESCONI and O. ANGELUCCI (*Gazzetta*, 1901, 31, ii, 302—312).—Although santonin resembles camphor in containing the group  $\cdot\text{CH}_2\cdot\text{CO}\cdot$ , it yields no *isonitroso*-compound under conditions similar to those employed in the formation of *isonitrosocamphor*. The authors have, however, succeeded in preparing a compound analogous to *pernitrosocamphor*.

*Pernitrososantonin*,  $\text{C}_{15}\text{H}_{18}\text{O}_4\text{N}_2$ , obtained by the action of amyl nitrite on santoninoxime, crystallises from ethyl acetate in pale yellow needles melting and decomposing at  $190^{\circ}$ . It is soluble in chloroform, acetone, and alcohol, and in chloroform solution has  $[\alpha]_D +169.92^{\circ}$ . Dilute acids do not dissolve it and it is not altered by continued boiling with dilute hydrochloric acid; with Liebermann's reagent, it gives a greenish-blue coloration, whilst concentrated hydrochloric acid, ammonia, or potassium hydroxide decomposes it, giving santonin and nitrous oxide.

*Santoninhydrazide*,  $(\text{C}_{15}\text{H}_{18}\text{O}_2\text{N})_2$ , prepared from the *pernitroso*-compound and hydrazine sulphate, crystallises from ethyl acetate in small, tetragonal octahedra, which melt and decompose at  $254^{\circ}$  and are

readily soluble in alcohol or chloroform and, to a less extent, in ether; with hydrochloric acid, it yields santonin and hydrazine.

*Santonin semicarbazone*,  $C_{16}H_{21}O_3N_3$ , prepared from the pernitroso-compound, semicarbazide hydrochloride, and sodium acetate, separates from ethyl acetate in almost white crystals, which melt and decompose at  $232^\circ$  and are soluble in alcohol and, to a slight extent, in benzene or ether.

*Dichlorosantonin*,  $C_{15}H_{18}O_3Cl_2$ , obtained by distilling nitrosyl chloride into well-cooled santonin, crystallises from ethyl acetate in white, rhombic prisms, which melt and decompose at  $160^\circ$  and are soluble in alcohol or chloroform and, to a slight extent, in ether; in chloroform solution, it has  $[\alpha]_D + 230.08^\circ$ .

From their results, the authors conclude that pernitrososantonin, and also the corresponding camphor derivative, have the constitution of a nitroso-oxime containing the grouping  $\cdot CH_2 \cdot \dot{C} : NO \cdot NO$ .

T. H. P.

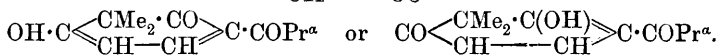
**Filicyl-*n*-butanone.** By RUDOLF BOEHM (*Annalen*, 1901, 318, 230—245. Compare Abstr., 1898, i, 40; 1899, i, 804).—*Filicyl-n-butanone*,  $C_{12}H_{16}O_4$ , obtained by heating filicic acid or flavaspodic acid with zinc dust and sodium hydroxide solution (15 per cent.), crystallises from xylene in rhombic plates and melts at  $95-97^\circ$ . It is soluble in all the ordinary solvents excepting light petroleum and water and dissolves in solutions of the alkali hydroxides and carbonates. The dilute alcoholic solution has a strongly acidic reaction, and is excessively bitter to the taste. The ketone unlike filicic acid, does not yield the characteristic aniline reaction, but it develops an intense reddish-brown coloration with ferric chloride. The *ammonium* and *copper* salts are crystalline. The *hydrate*,  $C_{12}H_{16}O_4 \cdot H_2O$ , slowly separates from solutions of the ketone in dilute acetone. The ketone is hydrolysed into filicic and butyric acids after 12 hours' boiling with zinc dust and sodium hydroxide. The *phenyl-carbamide*,  $C_{12}H_{15}O_3 \cdot O \cdot CO \cdot NHPh$ , obtained by mixing its generators in dry benzene, crystallises in rhombic or hexagonal plates and melts at  $115^\circ$ .

*Benzeneazofilicyl-n-butanone*,  $C_{12}H_{15}O_4 \cdot N_2Ph$ , produced from the ketone and an alcoholic solution of diazoaminobenzene, crystallises from alcohol in orange-yellow prisms and melts at  $137^\circ$ . *Benzenedisazofilicic acid*,  $C_8H_8O_3(N_2Ph)_2$ , prepared by substituting filicic acid for the above ketone in the preceding reaction, crystallises in dark red needles and melts at  $209^\circ$ .

Phenylhydrazine and filicyl-*n*-butanone interact to form the compound  $C_{24}H_{26}ON_4$ ; the substance crystallises in colourless prisms, melts at  $183-184^\circ$ , and is readily soluble in all the solvents except water.

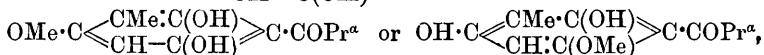
*Bromofilicyl-n-butanone*,  $C_{12}H_{15}O_4Br$ , results from the bromination of the ketone in ethereal solution; it crystallises in colourless, hexagonal plates and melts at  $85^\circ$ . Filicyl-*n*-butanone, when treated with potassium hypobromite, undergoes simultaneous hydrolysis and bromination, the products being tetrabromofilicic and butyric acids. The former of these acids separates in colourless crystals and melts at  $139-140^\circ$ .

Filicyl-*n*-butanone must be represented by one or other of the following formulæ,  $\text{OH}\cdot\text{C}\begin{smallmatrix} \text{CMe}_2\cdot\text{C}(\text{OH}) \\ \text{CH} \text{---} \text{CO} \end{smallmatrix} \text{C}\cdot\text{COPr}^a$ ,



G. T. M.

**Aspidinol.** By RUDOLF BOEHM (*Annalen*, 1901, 318, 245—252. Compare Abstr., 1898, i, 40, and the preceding abstract).—The melting point of pure aspidinol is 156—161°, and not 143° as previously indicated; the substance is a ketone having one or other of the following formulæ  $\text{OH}\cdot\text{C}\begin{smallmatrix} \text{CMe}\cdot\text{C}(\text{OMe}) \\ \text{CH}=\text{C}(\text{OH}) \end{smallmatrix} \text{C}\cdot\text{COPr}^a$ ,



*Dibenzoyl aspidinol*,  $\text{OMe}\cdot\text{C}_{11}\text{H}_{11}(\text{OBz})_2$ , obtained only from pure aspidinol by the Schotten-Baumann reaction, crystallises from alcohol in colourless prisms, melts at 108—109°, and is insoluble in solutions of the alkali hydroxides; it does not develop any coloration with ferric chloride.

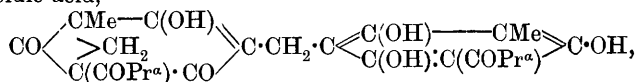
*Bromoaspidinol*,  $\text{C}_{12}\text{H}_{15}\text{O}_4\text{Br}$ , produced by brominating aspidinol in chloroform, crystallises in plates and prisms and melts at 95—96°. It dissolves in the organic solvents and in aqueous solutions of the alkali hydroxides; with ferric chloride, it develops a dark green coloration.

Aspidinol, when heated with concentrated sulphuric acid for a few minutes on the water-bath, decomposes, yielding methylphloroglucinol and butyric acid. *Methoxydihydroxymethylbenzene*,  $\text{OMe}\cdot\text{C}_6\text{H}_2\text{Me}(\text{OH})_2$ , and butyric acid are produced when aspidinol is digested for 10 hours with zinc dust and sodium hydroxide solution; the former substance crystallises from water in the monohydrated form,  $\text{C}_8\text{H}_{10}\text{O}_3\cdot\text{H}_2\text{O}$ , and when condensed with diazoaminobenzene it combines with two diazo-residues, yielding the compound  $\text{OMe}\cdot\text{C}_6\text{Me}(\text{OH})_2(\text{N}_2\text{Ph})_2$ , which crystallises in scarlet needles and melts at 204°. Aspidinol itself combines with only one diazo-residue, giving rise to *benzeneazo-aspidinol*,  $\text{C}_{12}\text{H}_{15}\text{O}_4\cdot\text{N}_2\text{Ph}$ , a compound crystallising from alcohol in scarlet needles and melting at 132°. G. T. M.

**Constitution of Albaspidin and Flavaspidic and Filixic Acids.** Two Noteworthy Reactions in the Phloroglucinol Series. By RUDOLF BOEHM (*Annalen*, 1901, 318, 253—308. Compare Abstr., 1898, i, 40; 1899, i, 32, 804, and preceding abstracts).—Flavaspidic acid is now considered to have the formula  $\text{C}_{24}\text{H}_{28}\text{O}_8$ ; it is obtained in two forms, the  $\alpha$ -modification crystallising from methyl or ethyl alcohol in lemon-yellow prisms melting at 92°, and the  $\beta$ -modification separating from benzene, xylene, or acetic acid solutions in flattened plates melting at 156°. Both varieties of the acid, when subjected to the Schotten-Baumann reaction in the presence of sodium hydroxide, give rise to a small amount of a colourless, crystalline product which is soluble in alkali hydroxide solutions and melts at 143—144°. The  $\beta$ -modification yields only a *tribenzoyl* derivative when this reaction is repeated with potassium hydroxide; the product

obtained in the form of an amorphous powder melts indefinitely at 150—160°, it is insoluble in alkali hydroxide solutions and develops a reddish-brown coloration with ferric chloride. *Diacetylflavaspidic acid*, prepared by the action of acetic anhydride on flavaspidic acid, crystallises from alcohol and melts at 142—143°; it is soluble in solutions of the alkali hydroxides and develops a coloration with ferric chloride. The compound  $C_{24}H_{26}O_7$  is obtained by the action of acetic anhydride on flavaspidic acid; it melts at 157°.

Flavaspidic acid, when heated with zinc dust and sodium hydroxide solution, undergoes simultaneous hydrolysis and hydrogenisation, 2 mols. of water and 1 mol. of hydrogen being required for the complete decomposition of 1 mol. of the substance. Under these conditions, two-thirds of the flavaspidic acid decomposes into filicyl-*n*-butanone, filicic acid, dimethylphloroglucinol, and butyric acid, whilst the remainder of the acid yields trimethylphloroglucinol, methylphloroglucinol, and butyric acid. The following constitutional formula for flavaspidic acid,



epitomises the foregoing results.

*Benzeneazomethylphloroglucinyl-n-butanone*,  $C_{11}H_{13}O_4 \cdot N_2Ph$ , obtained by treating an alcoholic solution of flavaspidic acid with diazoaminobenzene, is also formed by adding benzenediazonium sulphate to the alkaline solution of the acid. The azo-compound crystallises from glacial acetic acid in scarlet needles and melts at 181—182°; it is insoluble in the ordinary organic solvents, but readily dissolves in solutions of the alkali hydroxides and carbonates.

*Aminomethylphloroglucinol hydrochloride*,  $C_7H_9O_3N \cdot HCl \cdot 2H_2O$ , produced by reducing the preceding compound with stannous chloride, is isolated in the form of colourless or blue prisms, after removing the tin as sulphide and concentrating the solution in a vacuum over sulphuric acid; it melts indefinitely at 200—230°. At 55—60°, it loses water, yielding the anhydrous salt. The aqueous solution, when rendered alkaline with sodium hydroxide, develops a purple coloration which rapidly changes to blue.

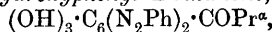
Albaspidin is now represented by the formula  $C_{25}H_{32}O_8$ ; it is shown to have the constitution of a methylenebisfilicyl-*n*-butanone by its partial synthesis from filicyl-*n*-butanone and formaldehyde. When condensed with diazoaminobenzene, albaspidin yields 2 mols. of benzeneazofilicyl-*n*-butanone, the linking methylene radicle being displaced by the azo-residues. Albaspidin, when condensed with phenylhydrazine, yields the compound  $C_{37}H_{40}O_4N_4$ ; this product separates from benzene and light petroleum in colourless, rhombic crystals and melts at 242°; it is probably a pyrazole derivative.

Albaspidin, when treated with zinc dust and sodium hydroxide, yields *n*-butyric and filicic acids, and an amorphous product which possibly contains 1 : 1 : 3-trimethylphloroglucinol.

Filicic acid,  $C_{35}H_{38}O_{12}$ , on boiling with alcohol for 3 hours, yields albaspidin; when heated with zinc dust and sodium hydroxide solution, it gives rise to filicyl-*n*-butanone, 1 : 3 : 5-trimethylphloroglucinol, *n*-butyric

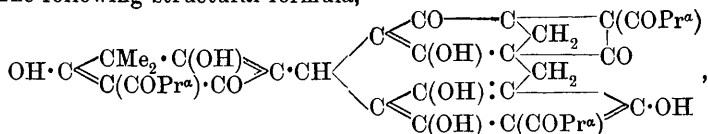


and filixic acids. By the action of diazoaminobenzene on filixic acid, *benzenediazo-1 : 3 : 5-hydroxyphenyl n-butanone*,



is obtained; it crystallises from glacial acetic acid in red needles melting at  $235^\circ$ , the crystals contain  $1\text{C}_2\text{H}_4\text{O}_2$ , which is removed on heating at  $100^\circ$ .

The following structural formula,



is considered to afford the simplest explanation of the reactions of filixic acid.

*Methylenebis-dimethylphloroglucinol*,  $\text{CH}_2[\text{C}_6\text{Me}_2(\text{OH})_3]_2$ , prepared by condensing dimethylphloroglucinol with formaldehyde in dilute hydrochloric acid solution, crystallises from alcohol in needles melting at  $252^\circ$ ; when heated with zinc dust and sodium hydroxide solution, it yields a mixture of di- and tri-methylphloroglucinols. The methylene radicle in this diphenylmethane derivative is again eliminated by the action of diazoaminobenzene in alcoholic solution with the formation of benzeneazodimethylphloroglucinol (m. p.  $200^\circ$ ). G. T. M.

**Euxanthic Acid.** By CARL GRAEBE, R. H. ADERS, and J. HEYER (*Annalen*, 1901, 318, 345—365. Compare Abstr., 1901, i, 85).—The greater portion of the work has already been published.

*Barium euxanthate*,  $\text{Ba}(\text{C}_{19}\text{H}_{17}\text{O}_{11})_2 \cdot 9\text{H}_2\text{O}$ , is a gelatinous, yellow precipitate obtained by treating the corresponding ammonium salt with barium chloride. The product of the acetylation of euxanthic acid with acetyl chloride consists of a mixture of the monoacetyl compound, and a derivative containing 3 or 4 acetyl groups. Ethyl euxanthate, when treated with acetyl chloride or acetic anhydride, yields a homogeneous product, *ethyl tetra-acetylexanthate*,  $\text{C}_{19}\text{H}_{11}\text{O}_{10}\text{EtAc}_4$ ; this compound crystallises from alcohol in white needles and melts at  $216^\circ$ . The acyl and alkyl derivatives of euxanthic acid give rise to euxanthone when hydrolysed either with cold concentrated sulphuric acid or with water in sealed tubes at  $150\text{--}180^\circ$ . G. T. M.

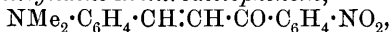
**Action of Alcoholic Ammonia on the  $\omega$ -Bromine Derivatives of *p*-Chlorophenyl Methyl Ketone and *p*-Bromophenyl Methyl Ketone.** By A. COLLET (*Bull. Soc. Chim.*, 1901, [iii], 25, 929—931).

—2 : 5-Di-*p*-chlorophenylpyrazine,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{C} \begin{array}{c} \text{N} \cdot \text{CH} \\ \text{CH} \cdot \text{N} \cdot \text{C} \end{array} \cdot \text{C}_6\text{H}_4\text{Cl}$ , obtained by the action of alcoholic ammonia on *p*-chlorophenyl bromomethyl ketone, crystallises in slightly yellow, nacreous plates melting at  $200\text{--}201^\circ$ . 2 : 5-Di-*p*-bromophenylpyrazine, obtained in a similar manner from *p*-bromo-phenyl bromomethyl ketone, crystallises in brilliant, yellow needles melting at  $235\text{--}236^\circ$ . Both compounds are dissolved, without decomposition, by hot concentrated nitric acid; they are also dissolved by concentrated sulphuric acid with the production of a red coloration which disappears on dilution with water. N. L.

**Derivatives of Acetophenone.** By HANS RUPE, A. BRAUN, and KASIMIR VON ZEMBRUSKI (*Ber.*, 1901, **34**, 3522—3526).—*Acetyl-m-aminoacetophenone*,  $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$ , crystallises from dilute alcohol in white prisms or needles and melts at  $128\text{--}129^\circ$ ; the *oxime*,  $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}\cdot\text{NOH}$ , separates from dilute alcohol in needles and melts at  $192\text{--}194^\circ$ . *m-Dimethylaminoacetophenone*,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$ , boils at  $148^\circ$  under 13 mm. pressure and solidifies to a crystalline mass which melts at  $42\text{--}43^\circ$ ; the *hydriodide*,  $\text{COMe}\cdot\text{C}_6\text{H}_4\cdot\text{NHMe}_2\text{I}$ , is sparingly soluble in water; the *hydrochloride* forms white needles; the *methiodide*,  $\text{COMe}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{I}$ , crystallises from water in broad tablets and melts at  $200\text{--}201^\circ$ ; the *oxime*,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CMe}\cdot\text{NOH}$ , crystallises from dilute alcohol in white needles and melts at  $78\text{--}79^\circ$ . *o-Nitro-p-dimethylaminoacetophenone*,  $\text{COMe}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{NMe}_2$ , crystallises from dilute alcohol in long, yellow needles with a steely lustre and melts at  $149\text{--}150^\circ$ . *o-Amino-p-dimethylaminoacetophenone hydrochloride*,  $\text{COMe}\cdot\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{NMe}_2\cdot\text{HCl}$ , crystallises from hydrochloric acid in white needles; the *stannochloride* forms yellowish-brown flakes; the *platinichloride* forms brown flakes; the *base* is a yellow oil which boils at  $220^\circ$  under 52—53 mm. pressure and does not solidify on cooling; the *acetyl* derivative crystallises from water in white needles and melts at  $146\text{--}148^\circ$ .

T. M. L.

**Chromophore Groups.** By HANS RUPE and D. WASSERZUG (*Ber.*, 1901, **34**, 3527—3531).—*m-Nitrobenzylidene-m-nitroacetophenone*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , crystallises from acetic acid in yellow needles and melts at  $210^\circ$ . *m-Aminobenzylidene-m-aminoacetophenone*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , is a yellow powder; the *hydrochloride* forms prismatic crystals; the *diacetyl* derivative crystallises from alcohol in small, white needles and melts at  $150^\circ$ ; the *base* forms a series of tetrazo-dyes containing the complex  $\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot$ . *p-Dimethylaminobenzylidene-m-nitroacetophenone*,



crystallises from acetic acid in minute, red needles and melts at  $165^\circ$ . *p-Dimethylaminobenzylidene-m-aminoacetophenone*,



forms a white, crystalline *hydrochloride* and a *platinichloride* which crystallises from hot water in large, brownish-red octahedra. *3:4-Dihydroxybenzylidene-m-nitroacetophenone*,  $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , crystallises from dilute alcohol, melts at  $217^\circ$ , and with mordants forms a very stable dye; the *diacetyl* derivative forms minute, white, silky needles and melts at  $179^\circ$ ; the *diethyl* ether crystallises from a mixture of alcohol and ether in minute, yellowish needles and melts at  $103^\circ$ .

T. M. L.

**Condensation Products of Phenylacetone [Benzyl Methyl Ketone] with Benzaldehyde.** By GUIDO GOLDSCHMIEDT and HANS KRCZMAR (*Monatsh.*, 1901, **22**, 659—669. Compare *Abstr.*, 1898, i, 31, and 1899, i, 140).—Benzyl methyl ketone and benzaldehyde condense under different conditions to form two isomeric ketones,  $\text{C}_{16}\text{H}_{14}\text{O}$  (*loc. cit.*). In this paper, the constitution of the two ketones is discussed, and the conclusion drawn that the ketone melting at  $71^\circ$ , obtained by using potassium hydroxide as condensing agent, is benzyl cinnamenyl ketone,

$\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}\cdot\text{CHPh}$ , whilst the ketone melting at  $53^\circ$ , obtained when hydrogen chloride is used, is stilbyl methyl ketone,



By reducing the ketone which melts at  $53^\circ$  (or the ketone,  $\text{C}_{16}\text{H}_{15}\text{OCl}$ , *loc. cit*), with sodium amalgam, a ketone [*dibenzyl methyl ketone*],  $\text{C}_{16}\text{H}_{16}\text{O}$ , is obtained as a yellowish oil which boils at  $311\text{--}312^\circ$  and solidifies in a freezing mixture; the *oxime*,  $\text{C}_{16}\text{H}_{17}\text{ON}$ , crystallises in white needles melting at  $134^\circ$ .

On reducing the ketone, which melts at  $71^\circ$ , with sodium amalgam, an oily ketone, boiling at  $234\text{--}238^\circ$  under 79 mm. pressure, is formed, and proves to be benzyl phenylethyl ketone (compare Spiegel, *Annalen*, 1883, 219, 34); the *oxime*,  $\text{C}_{16}\text{H}_{17}\text{ON}$ , melts at  $120^\circ$ .

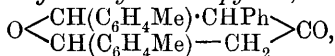
The ketone,  $\text{C}_{22}\text{H}_{18}\text{O}$  (m. p.  $86^\circ$ ), prepared by Goldschmiedt and Knöpfer (Abstr., 1900, i, 35) from dibenzyl ketone and benzaldehyde, is stilbyl benzyl ketone and not 1:2-diphenyltetrahydro- $\beta$ -naphthenone as previously suggested.

K. J. P. O.

**Condensation of Phenylacetone [Benzyl Methyl Ketone] with Aromatic Aldehydes.** By GUIDO GOLDSCHMIEDT and HANS KRCZMAŃ (*Monatsh.*, 1901, 22, 749—759. Compare Abstr., 1898, i, 31; 1899, i, 140; 1900, i, 35; and preceding abstract).—Phenylacetone and *p*-tolualdehyde, when shaken together for several days in the presence of dilute alcoholic potassium hydroxide, yield two substances, *p*-methylcinnamenyl benzyl ketone and 2:6-di-*p*-tolyl-3-phenyltetrahydro-1:4-pyrone.

*Benzyl p*-methylcinnamenyl ketone,  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Me}$ , crystallises in prisms melting at  $115^\circ$ , and with bromine gives *benzyl  $\alpha$ -methyl dibromocinnamenyl ketone*,  $\text{C}_{17}\text{H}_{16}\text{OBr}_2$ , which crystallises in needles melting at  $106^\circ$ . On warming an alcoholic solution of this substance, it is transformed into an isomeric  $\beta$ -compound, which crystallises in needles melting at  $89^\circ$ . With hydroxylamine hydrochloride, benzyl *p*-methylcinnamenyl ketone yields a compound,  $\text{C}_{17}\text{H}_{17}\text{ON}$ , which crystallises in needles melting at  $147^\circ$ , and is probably not an *oxime*, but 3-benzyl-5-*p*-tolylisooxazole.

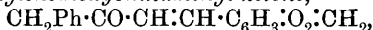
2:6-Di-*p*-tolyl-3-phenyltetrahydro-1:4-pyrone,



crystallises in needles melting at  $153\text{--}154^\circ$ .

*p*-Methoxycinnamenyl benzyl ketone,  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , prepared from anisaldehyde and phenylacetone, crystallises in leaflets melting at  $98\text{--}100^\circ$ , and with bromine yields a dibromide,  $\text{C}_{12}\text{H}_{16}\text{O}_2\text{Br}_2$ , which melts at  $116\text{--}117^\circ$ . *Benzyl p*-methoxybromocinnamenyl ketone,  $\text{C}_{12}\text{H}_{15}\text{O}_2\text{Br}$ , formed on boiling the dibromide with alcohol, crystallises in needles melting at  $85^\circ$ . On treating the ketone with hydroxylamine, a compound,  $\text{C}_{17}\text{H}_{17}\text{O}_2\text{N}$ , is formed, which melts at  $97\text{--}98^\circ$ .

*Benzyl 3:4-methylenedioxcinnamenyl ketone*,



prepared from piperonal and phenylacetone, crystallises in prisms melting at  $100\text{--}102^\circ$ ; with bromine, a dibromide,  $\text{C}_{17}\text{H}_{14}\text{O}_3\text{Br}_2$ , is obtained as needles melting at  $135^\circ$ , and with hydroxylamine, a compound,  $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}$ , which melts at  $137^\circ$ .

K. J. P. O.

**Derivatives of Anhydrobisdiketohydrindene.** By E. HOYER (*Ber.*, 1901, 34, 3269—3274).—*Anhydrobisdiketohydrindene phenylhydrazone*,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C:C \begin{smallmatrix} \diagup C_6H_4 \\ \diagdown CH_2 \end{smallmatrix} > C:N_2HPh$ , crystallises from chloro-

form in lustrous, blood-red needles and melts and decomposes at  $236^\circ$ .

The *benzylidene* derivative,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C:C \begin{smallmatrix} \diagup C_6H_4 \\ \diagdown C(CHPh) \end{smallmatrix} > CO$ , crystallises from glacial acetic acid in yellowish-red, lustrous needles and melts at  $205^\circ$ ; the analogous *cinnamylidene* derivative,  $C_{27}H_{16}O_3$ , separates from the same solvent in scarlet spangles and melts at  $243^\circ$ ; the *p-methoxybenzylidene* compound forms small, lustrous, reddish-brown needles melting at  $242^\circ$ .

The *methyl ether*,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C:C \begin{smallmatrix} \diagup C_6H_4 \\ \diagdown CH \end{smallmatrix} > C \cdot OMe$ , derived from the isodynamic form of anhydrobisdiketohydrindene and formed on saturating a methyl alcoholic solution of the latter with hydrogen chloride, crystallises in dark-red, lustrous needles melting at  $196^\circ$ ; the *ethyl ether* crystallises from alcohol in reddish-brown needles melting at  $159^\circ$ , and the *propyl ether* from acetone on diluting with water in dark-red, lustrous needles melting at  $135^\circ$ . When the propyl ether is boiled with bromine and a little iodine in glacial acetic acid solution, dibromoanhydrobisdiketohydrindene (Wislicenus and Kötze, *Abstr.*, 1889, 1067), and not a bromo-derivative of the ether, is formed; it melts at  $251^\circ$ , not at  $241$ — $242^\circ$ , and is only obtained with difficulty by brominating anhydrobisdiketohydrindene according to the directions formerly given (*loc. cit.*), although formed quantitatively by boiling with bromine and a little iodine in glacial acetic acid solution.

*Benzoylanhydrobisdiketohydrindene*,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C:C \begin{smallmatrix} \diagup C_6H_4 \\ \diagdown CH \end{smallmatrix} > C \cdot OBz$ , crystallises from benzene in dark red needles and melts and decomposes at  $210$ — $214^\circ$ .  
W. A. D.

**Methylation of Euxanthone and Alizarin with Dimethyl Sulphate.** By CARL GRAEBE and R. H. ADERS (*Annalen*, 1901, 318, 365—370).—Euxanthone, when treated at the ordinary temperature with dimethyl sulphate and sodium hydroxide, yields the yellow monomethyl ether described by Kostanecki, and a small quantity of the *dimethyl ether*,  $OMe \cdot C_6H_3 \begin{smallmatrix} \diagup CO \\ \diagdown O \end{smallmatrix} C_6H_3 \cdot OMe$ . The latter compound is more conveniently prepared by methylating the sodium derivative of the former product with the same reagents on the water-bath; it separates from dilute alcohol or light petroleum in colourless crystals and melts at  $149.5^\circ$ . This compound has already been obtained, but only in an impure state (Graebe and Ebrard, *Abstr.*, 1882, 1301). A colourless *monomethyl ether* of euxanthone is produced by hydrolysing the dimethyl derivative with hot concentrated sulphuric acid (90 per cent.); it resembles the corresponding monoethyl compound and dissolves in alcohol, chloroform, or solutions of the alkali hydroxides and melts at  $240^\circ$  (compare Herzig, *Abstr.*, 1891, i, 1349).

When heated with zinc dust, the dimethyl ether yields a very small amount of a red substance melting at  $90$ — $100^\circ$ , and probably consist-

ing of xanthene. The 2-methyl ether of alizarin is readily prepared from dimethyl sulphate in the presence of an alkali hydroxide. It was, however, not found possible to produce the dimethyl ether even by treating the red, insoluble *sodium* derivative of the monomethyl compound with boiling dimethyl sulphate or with methyl iodide at 180°.

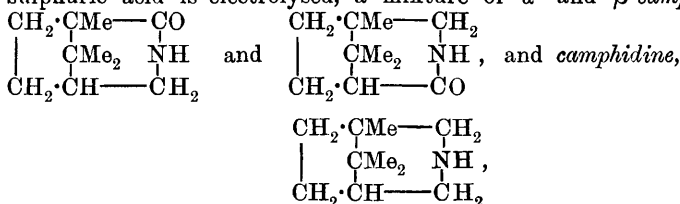
G. T. M.

**Derivatives of Camphor.** By MATTEO SPICA (*Gazzetta*, 1901, 31, ii, 286—288).—The author has obtained further evidence in support of the formula  $\text{CHPr}^\beta \begin{matrix} \text{CH} \cdot \text{CMe} \\ \text{CH}_2 \cdot \text{CH}_2 \end{matrix} \text{CO}$  for *isocamphor* by converting it into *m*-cymene.

The reduction of the oxime of *isocamphor* in alcoholic solution by means of sodium yields the corresponding *amine*,  $\text{C}_{10}\text{H}_{21}\text{N}$ , which is a colourless oil boiling at 201° under the ordinary pressure, and having a characteristic odour. The hydrochloride of the amine, when treated with sodium nitrite, yields tetrahydro*isocamphor*, whilst with potassium cyanate, the corresponding *carbamide*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_{19}$ , is obtained in the form of colourless crystals melting at 155°. On heating the phosphate of the amine, it yields a hydrogenised *hydrocarbon*, which is a yellowish liquid boiling at 169—171°. On treating this hydrocarbon with excess of an acetic acid solution of hydrogen bromide, it was found that the products, volatile in a current of steam, gave, on oxidation by the methods given by Wallach and by Baeyer, certain acids, which, by their melting points, are found to be identical with those yielded by the oxidation of *m*-cymene. The question is being further investigated with larger quantities of material.

T. H. P.

**Electrolytic Reduction of Camphorimide.** By JULIUS TAFEL and KARL ECKSTEIN (*Ber.*, 1901, 34, 3274—3286).—Camphorimide is best prepared by heating camphoric acid with 25 per cent. aqueous ammonia for 6 hours at 180°, and melts at 248° (uncorr.), not at 244—245° as formerly stated; its rotatory power depends on the concentration of its solutions. A solution of 20 grams in 100 c.c. of chloroform gave  $[\alpha]_D + 5.45^\circ$  at 23°; of 10 grams,  $[\alpha]_D + 4.3^\circ$  at 23°; and of 5 grams,  $[\alpha]_D + 1.55^\circ$  at 23°; with 2.5 grams, a rotation was no longer discernible. When a solution of the imide in 65 per cent. sulphuric acid is electrolysed, a mixture of  $\alpha$ - and  $\beta$ -camphidones,



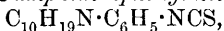
is obtained; as the two former are not further reduced on electrolysis in sulphuric acid solution, the camphidine must be formed by the simultaneous reduction of the two carbonyl groups of the imide.

*$\alpha$ -Camphidone* differs from its isomeride in yielding a sparingly soluble *picrate*, which crystallises from water in long, thin, anhydrous needles, melts at 190—192°, and on decomposition with alkali yields

the pure base; the latter melts at 230—232°, boils at 295° under 762 mm. pressure, crystallises from water, acetone, or light petroleum, and has  $[\alpha]_D - 37.2^\circ$  at 20° in a 10 per cent. benzene solution. It yields a sparingly soluble *platinichloride*, *phosphomolybdate*, *phosphotungstate*, *bismuthiodide*, and *mercurichloride*. It is not acted on by reducing agents, such as sodium in amyl alcoholic solution, or by boiling alcoholic sodium hydroxide, or aqueous barium hydroxide at 180°; the lactam ring is thus extraordinarily stable, and very different from that existing in the pyrrolidones.

*β-Camphidone*, purified initially by means of its picrate, and subsequently by crystallising from water, melts at 225°, and boils at 307—308° under 757 mm. pressure; it melts when heated with water, then dissolves to form a *hydrate*,  $C_{10}H_{17}ON, H_2O$ , which crystallises in long, colourless needles. *α-Camphidone* has  $[\alpha]_D + 66.5^\circ$  at 20° in a 10 per cent. benzene solution; like the *β*-compound, it is indifferent to reducing and hydrolytic agents, and yields similar double salts. The *picrate* crystallises from water or alcohol in stout, yellow needles and melts at 135—136°.

*Camphidine* forms a soft, crystalline mass of strongly camphor-like odour, melts at 186° (uncorr.), and boils at 209° (corr.) under 755 mm. pressure; in 10 per cent. benzene solution, it has  $[\alpha]_D + 23.9^\circ$  at 20°. Its aqueous solution is strongly alkaline; the *hydrochloride* is easily soluble in water and alcohol, and separates from the latter on adding ether in pike-shaped crystals; the *nitrate* crystallises from alcohol in needles melting and decomposing at 199° (uncorr.), and the *platinichloride* from water in thin, rectangular plates. The *picrate* is easily soluble in warm water. *Acetylcamphidine*,  $C_{12}H_{21}ON$ , forms a soft, crystalline mass, melts between 30° and 40° and boils at 290—291°; *nitrosocamphidine*,  $C_{10}H_{18}ON_2$ , crystallises from warm alcohol and gives Liebermann's reaction. *Camphidinephenylthiocarbamide*,



crystallises from alcohol in silky nodules and melts at 142—145° (uncorr.). With bromine in hydrobromic acid solution, camphidine yields a reddish-yellow perbromide. W. A. D.

**New Crystalline Component of Bergamot Oil.** By HUGO VON SODEN and WILHELM ROJAHN (*Chem. Centr.*, 1901, ii, 930; from *Pharm. Zeit.*, 46, 778—779).—The residue left after distilling bergamot oil contains not only bergapten but also a crystalline compound, *bergaptin*, which probably belongs to the aromatic series. It crystallises from light petroleum in leaflets, from ether in plates which resemble cubes, is easily soluble in alcohol, ether, or chloroform, and combines with bromine. The free acid obtained by treating bergapten with potassium hydroxide and acidifying with sulphuric acid changes spontaneously into bergapten. Bergapten contains neither phenolic nor methoxy-groups, but its carbon chain probably resembles that of coumarin. E. W. W.

**Empyreumatic Oil of Juniper. Cadinene.** By CATHELINEAU and JEAN HAUSSEUR (*Bull. Soc. Chim.*, 1901, [iii], 25, 931—933. Compare Abstr., 1901, i, 283).—The largest yield—about 8 per cent.—of cadinene hydrochloride is obtained from *unrectified* empyreumatic oil

of juniper, the possible decomposition of cadinene by heat being thus avoided. Full details of the process employed and the modifications introduced by the authors are given in the paper. N. L.

**Citrapten.** By ERNST SCHMIDT [with ADLUNG] (*Chem. Centr.*, 1901, ii, 809—810; from *Apoth.-Zeit.*, 16, 619—620. Compare Theulier, *Abstr.*, 1901, i, 218).—Citrapten,  $C_9H_4O_2(OMe)_2$ , obtained from the residue left after distilling lemon oil, crystallises in colourless needles or prisms, melts at 146—147°, sublimes easily, dissolves in alcohol forming a solution with a blue fluorescence, and is soluble in chloroform, slightly so in boiling water, ether, or light petroleum, and insoluble in cold dilute potassium hydroxide solution. The *nitro*-derivative crystallises in yellowish needles. The *dibromide*,  $C_{11}H_{10}O_4Br_2$ , forms yellowish needles, and melts at 250—260°. Citrapten is an acid anhydride or lactone and dissolves slowly in boiling dilute potassium hydroxide solution, but the acid which is precipitated from the alkaline solution on acidification is quickly reconverted into citrapten. Citrapten appears to be related to the dihydroxycoumarins and to be a derivative of phloroglucinol isomeric with dimethylæsculetin and dimethyldaphnetin. When fused with potassium hydroxide, it forms phloroglucinol and probably acetic acid. A *methyl ester*, prepared by the action of methyl iodide and sodium hydroxide on citrapten, forms colourless crystals, has acid properties, and melts at 215°.

A phenol, melting at 89°, was also isolated from the lemon oil residue. E. W. W.

**Essential Oils of Neroli and Petit Grain distilled in 1901.** By PAUL JEANCARD and C. SATIE (*Bull. Soc. Chim.*, 1901, [iii], 25, 934—936).—A number of specimens of oil of neroli and of petit grain distilled in 1901 after the severe winter of 1900—1901 were examined, and the analytical results compared with those yielded by specimens distilled in 1899 after a mild winter (*Abstr.*, 1900, i, 511). The sp. gr., rotatory power, solubility in alcohol, saponification numbers (hot and cold), esters, surface tension, and specific viscosity were determined. The sp. gr. of oil of neroli is slightly higher this year than previously, whilst the reverse is the case with oil of petit grain; the other figures show little variation. N. L.

**Storax.** By LEOPOLD VAN ITALLIE (*Chem. Centr.*, 1901, ii, 856—857; from *Ned. Tijds. Pharm.*, 13, 225—235).—The resin alcohol of storax storesinol,  $C_{16}H_{26}O_2$ , melts at 156—161°, has  $[a]_D + 13^\circ$ , is soluble in the lower alcohols, ether, chloroform, acetone, carbon disulphide, benzene or glacial acetic acid, but is insoluble in light petroleum. Its solution in concentrated sulphuric acid is red and has a green fluorescence. It dissolves in a 1 per cent. solution of sodium or potassium hydroxide, but is precipitated by excess of the alkali and is attacked with difficulty by molten alkalis, forming acetic and salicylic acids. By the action of nitric acid, it yields oxalic and picric acids and on distillation with zinc dust, gives benzene, toluene, and phenol. Neither an oxime nor a phenylhydrazone could be prepared. Mylius' styrogenin,  $C_{26}H_{40}O_3$ , prepared by treating storesinol with sulphuric acid, crystallises in colourless leaflets which show only slight polarisation; it is odourless, melts above 360°

and is soluble in chloroform, benzene or phenol, and readily so in hot alcohol but insoluble in ether or cold alcohol. By the action of hydroiodic acid on styrogenin a *compound*,  $C_{16}H_{26}O_3$ , is formed which crystallises in colourless leaflets and melts at about  $280^{\circ}$ .

Styrene is actually contained as such in storax and is not formed during the distillation in steam. A good storax contains about 2.4 per cent. insoluble in ether, 23.1 of free cinnamic acid, 14.0 of water, 22.5 of aromatic esters, 2.0 of styrene and vanillin, and 36.0 of resin, and gives an acid number 81, saponification number 179, ester number 98, and saponification number of mixture of esters and styrol 209. The total cinnamic acid is 47.3 per cent., the combined acid being 24.2, occurring partly in the resin and partly in the aromatic esters. E. W. W.

**American Storax.** By LEOPOLD VAN ITALLIE (*Chem. Centr.*, 1901, ii, 857; from *Ned. Tijds. Pharm.*, 13, 257—266).—American storax, prepared from *Liquidambar styraciflua*, L., is obtained in the form of a sticky, grey mass containing white, crystalline portions mixed with fragments of wood and bark. Its composition does not differ essentially from that of Asiatic storax. Coumarin, vanillin, styracin, phenylpropyl cinnamate, styrene, and an alcohol *styresinol*,  $C_{16}H_{26}O_2$ , have been isolated from it. Styresinol resembles storesinol in all its properties and may prove to be identical with it, but it has a specific rotatory power  $[\alpha]_D +52^{\circ}$ , whilst that of storesinol is  $+13^{\circ}30'$ .

E. W. W.

**Extraction of all the valuable Constituents from Digitalinum Germanicum.** By HEINRICH KILIANI (*Ber.*, 1901, 34, 3561—3562. Compare Abstr., 1891, 576; 1892, 1482; 1896, i, 58, 180).—Digitonine and *Digitalinum verum* can be simultaneously obtained from *Digitalinum germanicum* by precipitating the alcoholic extract with ether and working up the solution for *Digitalinum verum* and the precipitate for digitonin. For this purpose, the liquid is evaporated in a vacuum, the syrup dissolved in water, and all resinous matter removed by ether. The thick jelly of *Digitalinum verum* is then filtered off and washed with 5 per cent. alcohol. The filtrate contains digitalein.

The precipitate is dissolved by warming with 85 per cent. alcohol, and the digitonin then separates out on cooling. A. H.

**Digitonin and Digitogenic Acid.** By HEINRICH KILIANI and B. MERK (*Ber.*, 1901, 34, 3562—3577. Compare Abstr., 1892, 1483).—Digitogenin is best prepared by heating an alcoholic solution of digitonin with 2 parts of concentrated hydrochloric acid at  $100^{\circ}$  and may be recrystallised by adding boiling water to its solution in boiling 95 per cent. alcohol until it becomes opalescent and then allowing it to cool. By the action of zinc and sulphuric acid in acetic acid solution, it is converted into a *compound*,  $C_{80}H_{50}O_7$ , which crystallises in colourless needles melting at  $197$ — $198^{\circ}$ .

Digitogenic acid is best prepared by the oxidation of digitonin in acetic acid solution with chromic acid mixture. It is converted by nitric acid into two crystalline acids containing nitrogen. The more sparingly soluble of these "N-acid I,"  $C_{22}H_{28}O_8N_2$ , or  $C_{22}H_{30}O_8N_2$ , sinters at  $225^{\circ}$  and melts and decomposes at  $242^{\circ}$ . The *barium*



salt,  $C_{22}H_{26}O_8N_2Ba \cdot 8H_2O$ , is crystalline and sparingly soluble in water. The more soluble "N-acid II,"  $C_{44}H_{64}O_{15}N$ , crystallises with  $4H_2O$  in slender needles, becomes black at  $250^\circ$ , and melts at  $261-263^\circ$ . The zinc salt,  $C_{44}H_{60}O_{15}NZn_2$ , crystallises well with 8 or  $9H_2O$ , and is more readily soluble in cold than in hot water. The formation of a substance of this high molecular weight is either due to anhydride formation, or to the fact that the molecular weight of digitonin is higher than has been supposed.

*Acetyldigitogenic acid*,  $C_{28}H_{43}O_8Ac$ , is prepared by the action of acetic anhydride and crystallises with  $1H_2O$  in needles which soften at  $162-165^\circ$ . Acetyl chloride yields a compound melting at  $92^\circ$  which has not been investigated.

Digitogenic acid yields two oximes; the  $\alpha$ -oxime,  $C_{28}H_{45}O_8N$ , melts at  $175^\circ$ , but its composition differs from that assigned to it by Kiliani and Bazlen (Abstr., 1895, i, 65). The *magnesium* salt has the composition,  $C_{28}H_{43}O_8NMg \cdot 5H_2O$ . The  $\beta$ -oxime has the same composition as the  $\alpha$ -compound, but melts at  $105^\circ$ . Digitoic acid, which is formed from digitogenic acid with loss of carbon monoxide, also yields a *mono-oxime*,  $C_{27}H_{45}O_7N$ , which crystallises in plates, softens at  $234^\circ$ , and melts at  $244^\circ$ . Digitogenic acid, therefore, probably contains two ketonic groups, only one of which reacts directly with hydroxylamine. Digitic acid, prepared from oxydigitogenic acid by oxidation with potassium permanganate in alkaline solution, after having been previously boiled with neutral permanganate, was found to be converted by boiling dilute sulphuric acid into a new acid, whilst no other sample of the acid underwent a similar change. In order to throw light on this abnormality, similar experiments have been carried out with digitogenic acid. When the aqueous solution of a salt of this acid is boiled, one portion of the acid is converted into  $\beta$ -digitogenic acid, whilst a second portion is decomposed with formation of digitoic acid. When the acid is boiled with dilute sulphuric acid, a portion of it is also converted into  $\beta$ -digitogenic acid, and a second portion is decomposed with formation of a new substance, *gitonin acid*,  $C_{26}H_{44}O_6$ , which softens at  $220^\circ$  and melts at  $227^\circ$ . The *magnesium* salt,  $C_{26}H_{42}O_6Mg$ , crystallises in needles.

When digitogenic acid is oxidised by potassium permanganate at  $100^\circ$  it yields about 5—10 per cent. of the acid,  $C_9H_{14}O_4$ , or  $C_{18}H_{28}O_8$ , previously described by Kiliani (Abstr., 1893, i, 665). The monopotassium salt is dimorphous, crystallising in needles or compact, warty aggregations. A. H.

**Identity of Digitoflavone with Luteolin.** By HEINRICH KILIANI and O. MAYER (*Ber.*, 1901, 34, 3577—3578).—The digitoflavone obtained by Fleischer and Fromm (Abstr., 1899, i, 631) from *Digitalis* leaves is, as suggested by Diller and Kostanecki (Abstr., 1901, i, 476), identical with luteolin. The tribenzoate obtained by Fleischer's method melts at  $200-201^\circ$ , whilst Fleischer's compound melted at  $219^\circ$ . A tetrabenzoate can be prepared by Deninger's method (Abstr., 1895, i, 461), and this is identical with that obtained by A. G. Perkin (*Trans.*, 1896, 69, 206) from luteolin. Its dyeing properties also agree with those of luteolin. A. H.

**Scutellarin, a New Substance in Scutellaria and other Labiatae.** By HANS MOLISCH and GUIDO GOLDSCHMIEDT (*Monatsh.*, 1901, 22, 679—699).—When the leaves of *Scutellaria altissima* are boiled with 1 per cent. hydrochloric acid, their lower sides become covered with microscopic crystalline aggregates. Crystals of the same substance, scutellarin, separate when the aqueous extract of the leaves is acidified. It is found chiefly in the leaves; it occurs in *Scutellariae*, and in some other *Labiatae*, as *Galeopsis tetrahit* and *Tencrium chamædrys*.

*Scutellarin*,  $C_{21}H_{20}O_{12} \cdot 2\frac{1}{2}H_2O$ , is prepared by extracting the leaves and flowers of the plant with ten times the quantity of water and acidifying the extract with concentrated hydrochloric acid; the yield is less than 1 per cent. The acid filtrate from the scutellarin contains cinnamic and fumaric acids. Scutellarin crystallises in pale yellow needles, which darken at  $200^\circ$ , but do not melt at  $310^\circ$ . Lead acetate gives a red precipitate with the alcoholic solution, and ferric chloride an intense green coloration which becomes red on heating. Oxidising agents (chlorine, water, &c.) give an immediate green colour. Alkalis, ammonia, and alkali carbonates dissolve it with a deep yellow colour; these solutions reduce ammoniacal silver nitrate and Fehling's solution; acids reprecipitate scutellarin. Concentrated sulphuric acid dissolves it with a yellow colour. From the solution or suspension in acetic acid, concentrated mineral acids throw down deep yellow or orange, crystalline salts. The *acetyl* derivative melts and decomposes at  $267^\circ$ . When fused with potash, *p*-hydroxybenzoic acid and a substance, which crystallises in large plates, are formed.

Under the action of 30—40 per cent. sulphuric acid it is converted into *scutellarein*,  $C_{15}H_{10}O_6$ , which melts above  $300^\circ$ , dissolves in alkalis with a yellow colour, gives a reddish-brown tint with ferric chloride, an emerald-green colour with baryta water, and a yellowish-red precipitate with lead acetate. When fused with potash, *scutellarein* yields *p*-hydroxybenzoic acid and phloroglucinol (?). Scutellarin and *scutellarein* both appear to be flavone derivatives; the latter is probably represented by

the formula  $C_6H_3(OH)_2 \begin{array}{c} \text{O}-\text{C}\cdot\text{OH} \\ \parallel \\ \text{CO}\cdot\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{OH} \end{array}$  [ $(OH)_4 = 2:5:7:4$ ], and is

isomeric with the substance [kampherol (?)] described by A. G. Perkin and Wilkinson (*Proc.*, 1900, 16, 182), from which *p*-hydroxybenzoic acid and phloroglucinol are obtained on fusion with potash. K. J. P. O.

**Phoenicein, the Dye from Purple Wood (*Copaifera Bracteata*).** By ESTELLA KLEEREKOPER (*Chem. Centr.*, 1901, ii, 858; from *Ned. Tijds. Pharm.*, 13, 245—255).—The bark parenchyma cells of *Copaifera bracteata* contain phoenin,  $C_{14}H_{16}O_7$ , the glucoside of the leuco-compound of phoenicein, in solution; it is found principally in the core-wood; when boiled with hydrochloric acid it gives a red coloration, the glucoside being probably decomposed and the leuco-compound oxidised. Phoenin crystallises from water in minute, colourless needles or rods, and on exposure to the air becomes slightly violet; at  $100^\circ$ , it loses 6 per cent. of water and decomposes, forming a dye. Its solution in alkalis has a pale brown colour, but quickly becomes darker and decomposes, the dye being then no longer precipitated by acids. Phoenicein, prepared by boiling phoenin with methyl alcohol and hydrochloric acid and

treating with water, forms a red precipitate, which retains hydrochloric acid with great obstinacy. It is somewhat soluble in water containing a small quantity of hydrochloric acid, and with ammonia gives a violet-blue coloration. Purple wood yields about 2 per cent. of phoenicein.  
E. W. W.

**Scatole-red and Similar Colouring Matters of Urine.** By KARL RÖSSLER (*Chem. Centr.*, 1901, ii, 861—862; from *Centr. inn. Med.*, 22, 847—855).—When the indican test is applied to urine, especially when Obermeyer's method is employed, the liquid above the chloroform layer is often coloured in shades varying from brown to violet. As a rule, the dye is soluble in amyl alcohol, forming a brown solution. The same colouring matter may also be frequently obtained by treating the urine with fuming hydrochloric acid and extracting with amyl alcohol. Attempts to isolate indigo-red, urorosein, and scatole-red failed, however. By the action of hydrochloric acid on urine, neither indigo-red nor urorosein is formed, but the solubility of the dye and the fact that more is formed when scatole is introduced into the organism, render it probable that scatole-red is the colouring matter in this case. In order to detect scatole-red, 10 c.c. of urine are treated with an equal volume of fuming hydrochloric acid, and after remaining five minutes the mixture is shaken with amyl alcohol. If the extract, instead of showing a brownish-red colour, has a mixed colour with a tinge of blue, or if the urine is decomposed, a small quantity of lead acetate is added, and after removing indigo-red and indigo-blue from the filtrate by shaking with chloroform, the scatole-red is extracted by means of amyl alcohol.  
E. W. W.

**Furfurandicarboxylic Acid. Its Preparation, Salts, and Esters.** By P. A. YODER and BERNHARD TOLLENS (*Ber.*, 1901, 34, 3446—3462).—Furfurandicarboxylic acid may be obtained in 24 per cent. yield by heating mucic acid with twice its weight of concentrated sulphuric acid for 40 minutes in a glycerol-bath kept at a temperature of 133—137°, and is purified by conversion into its barium salt. The following salts are described: *sodium*,  $C_6H_2O_5Na_2 \cdot 4H_2O$ ; *potassium*, with 1.5 or  $2H_2O$ ; *strontium*, with  $6H_2O$ ; *magnesium*, with  $6H_2O$ ; *cadmium*, with  $4.5H_2O$ ; *copper*, with 2.5 or  $3H_2O$ ; *basic copper salt*,  $C_6H_2O_5Cu, Cu(OH)_2 \cdot 3H_2O$ . The *ammonium* and *lead* salts are anhydrous. The normal esters have the following melting and boiling points:

	M. p.	B. p.
Methyl.....	112°	154—156° under 15 mm. pressure
Ethyl.....	47	167—168 „ 16 „
<i>n</i> -Propyl.....	21—21.5	177—178 „ 15 „
<i>iso</i> -Propyl.....	42—42.5	156—159 „ 13 „
<i>n</i> -Butyl.....	37—38	186—190 „ 13 „
<i>iso</i> -Butyl.....	88	172—174 „ 13 „
<i>iso</i> -Amyl.....	37.5	207—211 „ 18 „

The authors cannot confirm Schmidt and Cobenzl's statement (*Abstr.*, 1884, 1125) that potassium furfurandicarboxylate is formed when potassium mucate is heated. Furfurandicarboxylic acid and a

number of its derivatives and allied substances have been treated with isatin and sulphuric acid, and the temperature at which a colour is produced noted.

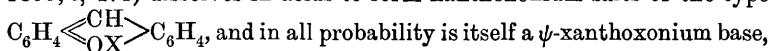
J. J. S.

**Phenoxozone Derivatives.** By HOMER W. HILLYER (*Amer. Chem. J.*, 1901, **26**, 361—372).—When dinitrophenoxozone, obtained by the action of picryl chloride on catechol (Abstr., 1900, i, 289), is reduced with tin and hydrochloric acid, *diaminophenoxozone*,  $C_6H_4 \cdot O_2 \cdot C_6H_2(NH_2)_2$ , is obtained, which crystallises in needles, melts and blackens at 198—200°, and acts both as a mono- and di-basic substance with chloroplatinic acid. Its *diacetyl* derivative crystallises in minute, lustrous scales and melts and darkens at 252·5—253°. The *benzoyl* derivative melts at 274—275°.

Dinitrophenoxozone dissolves in alcoholic sodium ethoxide to form a carmine-coloured solution, from which it is reprecipitated on addition of water. If sodium hydroxide is used instead of the ethoxide, *dinitrodihydroxyphenoxide*,  $OH \cdot C_6H_4 \cdot O \cdot C_6H_2(NO_2)_2 \cdot OH$ , is produced, which melts at 153—153·5°, is slightly soluble in water, and yields *ammonium*, *silver*, and *mono-* and *di-sodium* salts; its *dimethyl ether* melts at 119—120°. On reduction with tin and hydrochloric acid, a substance is produced which furnishes a light violet hydrochloride.

When 3-nitrocatechol is treated with picrylchloride, a yellow, crystalline condensation product is obtained. Picryl chloride reacts with pyrogallol with formation of *dinitrohydroxyphenoxozone*,  $OH \cdot C_6H_3 \cdot O_2 \cdot C_6H_2(NO_2)_2$ , which crystallises from acetic acid in brown, transparent spikes, melts and decomposes at 258—258·5°, and is readily soluble in nitrobenzene, glacial acetic acid, or acetone, and fairly so in alcohol, phenol, or ethyl acetate, but only sparingly so in hot water. On reduction with tin and hydrochloric acid, a *base* is obtained which crystallises in needles, melts at 252—253°, and is soluble in alcohol or acetone. E. G.

**Carboxonium and Carbothionium Salts.** By ALFRED WERNER (*Ber.*, 1901, **34**, 3300—3311).—Xanthhydrol (Meyer and Saul, Abstr., 1893, i, 471) dissolves in acids to form xanthoxonium salts of the type



$C_6H_4 \begin{array}{c} \text{CH(OH)} \\ \diagup \quad \diagdown \\ \text{O} \end{array} C_6H_4$  (compare Collie and Tickle, Trans., 1899, **75**, 710, and Kehrman, Abstr., 1900, i, 61; 1901, i, 484); the simple salts are very soluble and cannot be isolated, but double salts, like the crystalline *ferrichloride*,  $C_{13}H_9OCl_4Fe$ , *perbromide*,  $C_{13}H_9OBr_3$ , *platinichloride*, and *mercurichloride* are readily obtained; the latter forms long, yellow, spear-like prisms. Pheno- $\alpha$ -naphthoxanthhydrol also yields salts of the type  $C_6H_4 \begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{OX} \end{array} C_{10}H_6$ ; the reddish-brown *ferrichloride*,  $C_{17}H_{11}OCl_4Fe$ , and the brown *perbromide* were prepared.

On oxidising benzyldiene- $\beta$ -dinaphthyl oxide in acetic acid solution containing hydrochloric acid with manganese dioxide and adding ferric chloride, the *salt*,  $C_{10}H_6 \begin{array}{c} \text{CPh} \\ \diagup \quad \diagdown \\ \text{OCl} \cdot FeCl_3 \end{array} C_{10}H_6$ , separates and can be crystallised from glacial acetic acid in long, orange needles; on

dissolving this in acetone containing water, colourless, concentric aggregates of flat needles separate, which melt at  $248^{\circ}$  and consist of the *anhydride*  $\left(\text{O} \begin{smallmatrix} \text{C}_{10}\text{H}_5 \\ \text{C}_{10}\text{H}_6 \end{smallmatrix} \right)_2 \text{CPh}$ , of the  $\psi$ -base. This dissolves in acids, yielding salts, which, however, are best obtained by dissolving the anhydride in glacial acetic acid and adding the acid; the *perbromide*,  $\text{C}_{27}\text{H}_{17}\text{OBr}_3$ , forms lustrous, golden leaflets, which, on rubbing, change to a reddish-yellow powder. On warming the above-mentioned ferrichloride with absolute alcohol, the *ethoxide*,  $\text{C}_{10}\text{H}_8 \begin{smallmatrix} \text{CPh}(\text{OEt}) \\ \text{O} \end{smallmatrix} \text{C}_{10}\text{H}_8$ , of the  $\psi$ -base is obtained, which crystallises from benzene in white, acutely truncated prisms melting at  $218\text{--}219^{\circ}$ .

The reduction of xanthone, which, with zinc dust and hydrochloric acid yields dixanthylene (Gurgenjanz and Kostanecki, Abstr., 1896, i, 52), gives, with zinc and hydrobromic acid, *dixanthoxonium zincobromide*,  $\text{BrO} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} \cdot \text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{OBr} \cdot \text{ZnBr}_2$ ; the *ferrichloride* obtained from this is beautifully crystalline. Dixanthylene itself can readily be converted into *dixanthoxonium nitrate*,  $(\text{C}_{13}\text{H}_8\text{O} \cdot \text{NO}_3)_2$ , by suspending it in benzene and saturating with nitrous fumes at  $60\text{--}70^{\circ}$ ; the nitrate forms stout, brown crystals with a bluish lustre, and is converted by hydrobromic acid into the corresponding *bromide*, which readily dissolves in water and yields a black, additive compound with alcohol.

Pyrone, like dimethylpyrone, yields crystalline salts; the *platini-chloride* forms large, flat, amber-yellow crystals. Fluorescein, rhodamine, rosamine, and pyronine dyes are probably oxonium salts.

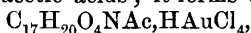
Thioxanthone, on reduction with zinc and alcoholic sodium hydroxide, yields *thioxanththydrol*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}(\text{OH}) \\ \text{S} \end{smallmatrix} \text{C}_6\text{H}_4$ , a  $\psi$ -base which crystallises from light petroleum in needles, melts at  $150^{\circ}$ , and yields salts analogous to those of xanththydrol; the *perbromide*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \\ \text{SBr}_3 \end{smallmatrix} \text{C}_6\text{H}_4$ , forms copper-red, lustrous leaflets. The chromophoric character of the thionium group is apparently greater than that of the oxonium radicle.

W. A. D.

**Amine derived from the supposed Dinaphthylene Glycol.** By R. FOSSE (*Compt. rend.*, 1901, 133, 639—641. Compare this vol., i, 604, 643).—The author shows that the so-called bromide and amine prepared from the supposed dinaphthylene glycol by Rousseau (Abstr., 1884, i, 180) are in reality dinaphthoxanthone derivatives and respectively identical with bromodinaphthoxanthone and bisdinaphthoxanthone-amine obtained from dinaphthoxanthone (*loc. cit.*). K. J. P. O.

**Hyoscine and Atroscine.** By OSWALD HESSE (*J. pr. Chem.*, 1901, [ii], 64, 353—386).—A detailed description of the salts and derivatives of hyoscine and atroscine, which shows the correctness of the author's opinion (Abstr., 1897, i, 232, and 1900, i, 51) that optically active scopolamine (see Schmidt, Abstr., 1895,

i, 158) is identical with hyoscyne. Hyoscyne dissolves in 9.5 parts of water at 15° and forms the following salts in addition to those previously described (*loc. cit.*, and also Abstr., 1896, i, 656); the *hydrochloride*,  $C_{17}H_{21}O_5N \cdot HCl$ , crystallises from acetone and melts at 197°; the *hydrobromides* crystallise with  $\frac{1}{2}H_2O$ , with  $H_2O$ , and with  $2H_2O$ ; the *hydriodide* crystallises from alcohol in compact prisms with  $H_2O$  and melts at 197° when anhydrous; the *salicylate* is a syrup and the *sulphate*,  $(C_{17}H_{21}O_4N)_2 \cdot H_2SO_4 \cdot 2H_2O$ , crystallises in microscopic needles. The rotation of hyoscyne has not yet been accurately determined; it seems, however, to be about  $[\alpha]_D -33^\circ$ . *Acetylhyoscyne*,  $C_{17}H_{20}O_4N \cdot Ac$ , obtained by the action of acetic anhydride on hyoscyne hydrobromide, is a syrup, which, when hydrolysed with barium hydroxide, yields oscine, and atropic and acetic acids; it forms an *aurichloride*,



which crystallises in leaflets melting at 148° and a *hydrobromide* which is an amorphous powder with  $[\alpha]_D -8.9^\circ$ . Hyoscyne methiodide melts at 208° [not at 215° as given by Schmidt for scopolamine methiodide (*loc. cit.*)] and has  $[\alpha]_D -13.8^\circ$ , the *methochloride* crystallises, with  $H_2O$ , in large, colourless prisms, melts, when anhydrous, at 189° and forms an amorphous *platinichloride* and an *aurichloride* melting at 143°, the *methobromide* is obtained in large, colourless crystals with  $H_2O$  and melts at 214° when anhydrous. Hyoscyne ethiodide has the properties of scopolamine ethoxide (Schmidt, *loc. cit.*), the *ethobromide* and *ethochloride* are also described.

Atroscine dissolves in 37 parts of water at 18° and the melting points of its anhydrous hydrobromide and hydriodide are now given as 181° and 192° respectively. *Acetylattroscine*,  $C_{17}H_{20}O_4N \cdot Ac$ , is a colourless syrup soluble in hydrochloric acid and precipitated by alkalis, is inactive, and forms an *aurichloride*, which begins to sinter at 120° and melts at 140°, and a *platinichloride*, which is obtained with  $2H_2O$ , as an amorphous precipitate melting at about 165°. The *methiodide* crystallises, with  $H_2O$ , in colourless, lustrous prisms and, when anhydrous, melts at 202°, the *methobromide* crystallises, with  $H_2O$ , in compact prisms and melts at 207° when anhydrous, the *methochloride* crystallises, with  $H_2O$ , in lustrous prisms, and forms an *aurichloride* melting at 146°; these, when treated with moist silver oxide, give a solution of the *methohydroxide*, which is strongly alkaline. The *ethiodide* crystallises in octahedra, melts at 170°, and forms an *aurichloride* melting at 124°. Atroscine is best obtained from hyoscyne hydrobromide by treatment with sodium hydroxide.

The paper concludes with an account of the pharmaceutical uses of hyoscyne, atroscine, and "scopolamine."

R. H. P.

**Diclytra Spectabilis.** By JOHANNES GADAMER (*Chem. Centr.*, 1901, ii, 814; from *Apoth. Zeit.*, 1901, 16, 621. Compare Battandier, *Compt. rend.*, 1892, 114, 1122).—Protopine (macleyine, fumarine),  $C_{20}H_{19}O_5N$ , extracted from the roots of *Diclytra spectabilis* by means of alcohol containing acetic acid, separates from chloroform and ethyl acetate in dull, crystalline aggregates, melts at 201–202°, and forms an anhydrous hydrochloride (compare Hopfgartner, Abstr., 1898, i,

606). Protopine prepared from *Chelidonium majus* also melts at 201—202°. The roots of *Corydalis cava* do not appear to contain protopine. E. W. W.

**Cinchotinesulphonic Acid.** By THEODOR SCHMID (*Monatsh.*, 1901, 22, 803—812).—When heated with potassium hydroxide at 100°, cinchotinesulphonic acid is not changed; when heated at 184° with potassium hydroxide in the presence of amyl alcohol, it yields a base,  $C_{19}H_{20}N_2$ , the *picrate* of which melts at 183°. At 140°, the sulphonic acid gives *hydroxycinchotine*,  $C_{19}H_{24}O_2N_2$ ; the *picrate* melts at 156°. On oxidation of cinchotinesulphonic acid or hydroxycinchotine by chromic acid, cinchonic acid is formed, a fact which shows that the sulphonic acid group is probably in the so-called second half of the cinchotine molecule.

Hydroquininesulphonic acid is not attacked by potassium hydroxide at 100°, but by hydrochloric acid is hydrolysed to hydroquinine and sulphuric acid. K. J. P. O.

**Electrolytic Reduction of Strychnine and of Brucine.** By JULIUS TAFEL and KURT NAUMANN (*Ber.*, 1901, 34, 3291—3299).—The electrolytic reduction of strychnine in sulphuric acid solution using lead electrodes and a closed vessel (compare Abstr., 1898, i, 703; 1900, ii, 588) gives tetrahydrostrychnine almost entirely (70 per cent.) at a temperature of  $-2^\circ$  to  $1^\circ$ ; at 35—43°, nearly equal quantities of tetrahydrostrychnine and strychnidine are obtained, the latter being produced from the former by the separation of water brought about by the sulphuric acid at the higher temperature.

A similar reduction of brucine at  $15^\circ$  gave principally a *tetrahydrobrucine*,  $OH \cdot CH_2 \cdot C_{20}H_{20}ON(OMe)_2 \cdot NH$ , which crystallises from methyl alcohol in colourless prisms, begins to decompose at 185°, and ultimately melts at 200—201° to a yellow liquid; the reduction at temperatures above  $15^\circ$  is more rapid, but a crystalline product cannot then be isolated, substances extremely sensitive to the action of the air being formed. *Tetrahydrobrucine hydrochloride*,  $C_{23}H_{30}O_4N_2 \cdot HCl$ , crystallises from alcohol in thin, colourless leaflets; the *platinichloride*, *mercurichloride* and *picrate* are amorphous; the *dihydrochloride*,  $C_{23}H_{30}O_4N_2 \cdot 2HCl$ , separates from hot alcohol in colourless crystals which rapidly become greenish in the air. With nitrous acid, tetrahydrobrucine does not yield a nitrosoamine.

*Brucidine*,  $C_{20}H_{20}ON(OMe)_2 \leq \begin{matrix} CH_2 \\ | \\ N \end{matrix}$ , which is not formed during the electrolytic reduction of brucine, is obtained by heating tetrahydrobrucine at 220° in a stream of hydrogen for 40 minutes; it crystallises from ethyl acetate in nodules of silky needles, becomes brownish at 195° and melts at 198°. The *hydrochloride* is similar to that of tetrahydrobrucine.

Unlike strychnidine and tetrahydrostrychnine, which can be readily distinguished from one another by colour reactions in acid solution with ferric chloride, chromic acid, and nitrous acid, brucidine and tetrahydrobrucine give very similar indications with these reagents.

The electrolytic reduction of quinine, cinchonine, and cinchonidine, did not give crystalline products. W. A. D.

**Transformation of Pyrroles into Pyrrolines.** By LUDWIG KNORR and PAUL RABE [and, in part, H. BUFLEB and C. JAKOBI] (*Ber.*, 1901, **34**, 3491—3502).—Better yields of pyrroline are obtained by reducing pyrroles with zinc and hydrochloric acid than by using zinc and acetic acid, as recommended by Ciamician and Dennstedt (*Abstr.*, 1883, 82).

2:5-Dimethylpyrroline,  $\begin{array}{c} \text{CH}=\text{CMe} \\ | \\ \text{CH}_2\cdot\text{CHMe} \end{array} > \text{NH}$  or  $\begin{array}{c} \text{CH}\cdot\text{CHMe} \\ | \\ \text{CH}\cdot\text{CHMe} \end{array} > \text{NH}$ , obtained from 2:5-dimethylpyrrole, boils at 106° (corr.) under 736 mm. pressure, and has a sp. gr. 0.8369 at 20°/4°, and  $n_D$  1.4401 at 20°; the *platinichloride* forms orange-coloured prisms or rhombs, and melts and decomposes at 198°; the *aurichloride* melts and sinters at 68—69°, and decomposes at 150°; the *picrate* melts at 105°, and the characteristic *picrolonate* at 130° with decomposition.

2:4-Dimethylpyrroline boils at 121° (corr.) under 752 mm. pressure, and has a sp. gr. 0.8554 at 20°/4°, and  $n_D$  1.4493 at 20°. The *platinichloride* (needles) melts at 185°, the *picrate* (prisms) at 102—104°, and the *picrolonate* at 225°; 1:2:4-trimethylpyrroline is a highly deliquescent, crystalline mass, but gives an *aurichloride* crystallising in orange-coloured needles, and melting at 251°.

1:2:5-Trimethylpyrroline boils between 105° and 120°; the fraction between 105° and 110° has a sp. gr. 0.8138 at 20°/4°, and  $n_D$  1.4334 at 20°; that boiling at 110—115° (largest fraction) has a sp. gr. 0.8131 at 20°/4°, and  $n_D$  1.4365 at 20°, and that boiling at 115—120° has a sp. gr. 0.8206 at 20°/4°, and  $n_D$  1.4422 at 20°. The three fractions have a practically identical composition and yield identical salts; the *platinichloride* (brown, irregular plates) melts at 150°; the *aurichloride* (rosettes of plates) melts and decomposes at 115°, the *picrate* (needles) at 195—205°, and the *picrolonate* (prisms) at 180—190°. The *methiodide* forms white scales, is very hygroscopic, and melts at about 310°.

Pyrroline (compare Ciamician and Dennstedt, *loc. cit.*) boils at 90° (corr.) under 748 mm. pressure, and has a sp. gr. 0.9097 at 20°/4°, and  $n_D$  1.4664 at 20°; the *platinichloride* melts and decomposes at 182°, and the *picrolonate* forms yellow, rhombic plates, darkens at 235°, and melts and decomposes at 260°.

The foregoing pyrrolines are reduced by heating with hydriodic acid and phosphorus to pyrrolidines, but the yield is generally poor.

2:4-Dimethylpyrrolidine boils at 115—117° (corr.) under 753 mm. pressure, and has a sp. gr. 0.8297 at 20°/4°, and  $n_D$  1.4325 at 20°; the *platinichloride* (needles) melts at about 210°, the *picrate* at 116—117°, and the *picrolonate* at 227°.

1:2:5-Trimethylpyrrolidine *picrate* melts at 163°, the *picrolonate* at 193°, and the *methiodide* at 310° (compare Tafel and Neugebauer, *Abstr.*, 1890, 1000, and Merling, *Abstr.*, 1891, 1506). W. A. D.

**isoConiine.** By ALBERT LADENBURG (*Ber.*, 1901, **34**, 3416).—Polemical (compare *Abstr.*, 1897, i, 173). J. J. S.

**Action of Iodine on a Pyridine Solution of Quinol.** By GIOVANNI ORTOLEVA and G. DI STEFANO (*Gazzetta*, 1901, **31**, ii, 256—265. Compare *Abstr.*, 1900, i, 558 and 592).—By the action of



iodine on a solution of quinol in a mixture of alcohol and pyridine, or by the interaction of aqueous quinol and excess of pyridine hydriodide, or by the addition of concentrated hydriodic acid to a pyridine solution of quinol, an *additive* compound,  $\text{OH} \cdot \text{C} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \text{CH} \cdot \text{CH} \end{smallmatrix} \text{CO} \cdot \text{C}_5\text{NH}_5\text{I}$ , is obtained; it crystallises from water in long, stout needles, which blacken at  $240^\circ$  and melt at  $254^\circ$ . It dissolves in alcohol, and silver nitrate precipitates the iodine quantitatively from its aqueous solution. Alcoholic potassium hydroxide dissolves it, giving a violet colour, whilst its solutions in aqueous alkali hydroxides and carbonates are deep red and, when acidified with sulphurous acid, yield the unaltered compound. Its *acetyl* derivative,  $\text{C}_{11}\text{H}_9\text{O}_2\text{NIac}$ , crystallises from water in large, yellowish plates containing  $1\text{H}_2\text{O}$ , and from chloroform in long, flat, faintly yellow needles which melt at  $165\text{--}168^\circ$ , and are soluble in acetic acid.

The corresponding *chloro*-compound,  $\text{C}_6\text{H}_4\text{O}_2 \cdot \text{C}_5\text{NH}_5 \cdot \text{HCl}$ , obtained by the action of concentrated hydrochloric acid on a pyridine solution of quinol, or in quantitative yield by the action of hydrochloric acid on the iodo-compound, crystallises from water in thin needles melting at  $223\text{--}225^\circ$ , and dissolving in alcohol.

The *bromo*-compound,  $\text{C}_6\text{H}_4\text{O}_2 \cdot \text{C}_5\text{NH}_5 \cdot \text{HBr}$ , prepared in a similar manner, forms brownish-yellow needles melting at  $230^\circ$ , and has properties analogous to those of the other two compounds.

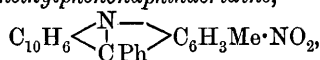
T. H. P.

**Action of Pyridine Bases on Tetrahalogenated Quinones. Quinol Derivatives.** By HENRI IMBERT (*Compt. rend.*, 1901, 133, 633—634. Compare Abstr., 1901, 651, 652).—Pyridyldichlorohydroxyquinone,  $\text{C}_5\text{NH}_4 \cdot \text{C}_6\text{Cl}_2\text{O}_2(\text{OH})$  (*loc. cit.*), is converted by a boiling concentrated aqueous solution of sulphur dioxide into *pyridylchlorohydroxyquinolsulphonic acid*,  $\text{C}_5\text{NH}_4 \cdot \text{C}_6\text{Cl}(\text{OH})_3 \cdot \text{SO}_3\text{H}$ , which crystallises from water in pearly needles; its aqueous solution reduces Fehling's solution and gives a dark red coloration with ferric chloride, a blue coloration with ferrous sulphate, and a bright red coloration with platinic salts. The alkaline solutions rapidly darken on exposure to air.

The mother liquor, from which the compound just mentioned has separated, deposits, on addition of sodium acetate, *pyridyldichlorohydroxyquinol sulphate*,  $\text{C}_5\text{NH}_4 \cdot \text{C}_6\text{Cl}_2(\text{OH})_3 \cdot \text{H}_2\text{SO}_4$ ; this substance forms colourless crystals, which rapidly become red in contact with air, or on exposure to light. The aqueous solution becomes red on treatment with oxidising agents and reduces Fehling's solution.

K. J. P. O.

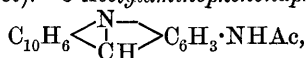
**Naphthacridine Derivatives.** FRITZ ULLMANN (D.R.-P. 117472. Compare Abstr., 1900, i, 360).—*5-Phenyl-3-methylphenonaphthacridine*,  $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{C}_{\text{Ph}} \end{smallmatrix} \text{C}_6\text{H}_4\text{Me}$ , produced by condensing benzylidene-*p*-toluidine with  $\beta$ -naphthol, is a yellow, crystalline powder melting at  $213^\circ$ ; it has slightly basic properties and forms a yellow nitrate and sulphate.

*5-m-Nitrophenyl-3-methylphenonaphthacridine,*

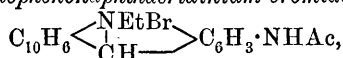
prepared in a similar manner from *m*-nitrobenzylidene-*p*-toluidine, separates from benzene or glacial acetic acid in pale yellow crystals and melts at 273°.

G. T. M.

**Preparation of Acridinium Colouring Matters.** FRITZ ULLMANN (D.R.-P. 118439. Compare Abstr., 1900, i, 361, 689, and preceding abstract).—3-Acetylaminophenonaphthacridine,



produced by heating acetyl-*p*-phenylenediamine, trioxymethylene and  $\beta$ -naphthol at 180°, crystallises from alcohol in yellow, felted needles and melts at 255°.

*Ethyl-3-acetylaminophenonaphthacridinium bromide,*

prepared by heating the preceding substance with ethyl bromide in chloroform or benzene solution at 150°, yields a yellow solution and on hydrolysis furnishes a base forming red, soluble salts. The salts of the base dye cotton mordanted with tannin in reddish shades, whilst those of the acetyl derivative give orange-yellow tints. These quaternary salts are not affected by ammonia or the alkali carbonates; alkali hydroxides, however, decompose them, setting free the colour base as a red precipitate.

2-Amino-3-methyl-5-phenylphenonaphthacridine yields an acetyl derivative,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{Ph} \end{array} \text{C}_6\text{H}_2\text{Me}\cdot\text{NHAc}$ , melting at 255—256°, the latter compound, when heated at 160—170° with ethyl bromide in chloroform solution, gives rise to a quaternary ethobromide, which, on hydrolysis, furnishes the corresponding amino-ethobromide. The dyeing properties of these quaternary salts are similar to those of the analogues just described.

G. T. M.

**Synthesis of Oxazolidines by the Action of Aldehydes on Hydramines.** By LUDWIG KNORR and HERMANN MATTHES (*Ber.*, 1901, 34, 3484—3489).—The following compounds were prepared by boiling equivalent quantities of the hydramine,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NHR}$ , and aldehyde in ethereal solution for several hours in presence of potassium carbonate; they are easily hydrolysed by aqueous acids and alkalis, and hence the only salts readily obtainable are the picrates.

2-Phenyl-3-methyloxazolidine,  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{NMe} \end{array} \text{CHPh}$ , obtained from benzaldehyde and methylhydroxyethylamine, boils at 240° under 746 mm., and yields a picrate which melts indefinitely at 110°, and is converted by recrystallisation into methylhydroxyethylamine picrate. On oxidation with chromic acid, it gives sarcosine and benzoic acid.

2-Phenyloxazolidine, obtained from benzaldehyde and hydroxyethylamine, boils at 284° under 748 mm. pressure.

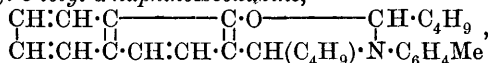
2-Phenyl-3-isobutyloxazolidine boils at 266—268° under 754 mm. pressure, the *picrate* is yellow and melts at about 110°.

2:3-Dimethyloxazolidine, obtained from acetaldehyde and methylhydroxyethylamine, boils at 109° under 758 mm. pressure and yields a *picrate* melting indefinitely at 75°; when hydroxyethylamine is used, 2-methyloxazolidine is obtained, which boils at 140—142° under 748 mm. pressure and gives a *picrate* melting at about 75°.

3-Methyloxazolidine,  $\begin{array}{c} \text{CH}_2 \text{---} \text{O} \\ | \quad \diagup \\ \text{CH}_2 \cdot \text{NMe} \end{array} \text{CH}_2$ , is obtained only in poor yield from formaldehyde and methylhydroxyethylamine and boils at 100° under 735 mm. pressure; the *picrate* melts at 152°. W. A. D.

**Synthesis of  $\alpha$ -Naphthoisoxxazine Derivatives.** By MARIO BETTI (*Gazzetta*, 1901, 31, ii, 209—215. Compare Abstr., 1901, i, 753).—The 2:3:4-triphenyl-1:3- $\alpha$ -naphthoisoxxazine, prepared by the interaction of benzylidene- $\alpha$ -naphthol and benzaldehyde (*loc. cit.*), can be obtained directly from  $\alpha$ -naphthol, benzaldehyde, and aniline; it crystallises from benzene in small scales, which turn yellow at 150° and melt at 158—160°. The melting point varies very considerably with the solvent from which crystallisation takes place; thus, by heating with acetic anhydride, no acetyl compound is obtained, but the original substance is recovered, the melting point being raised to 195—197°.

2:4-Dibutyl-3-tolyl- $\alpha$ -naphthoisoxxazine,



prepared from  $\alpha$ -naphthol, *p*-toluidine, and valeraldehyde, separates from alcohol in shining, white needles melting at 191°. With cold ferric chloride it gives no colour, but on boiling, an intense carmine coloration is produced which does not disappear on cooling. T. H. P.

**Preparation of Alkylhydrazines.** By ROBERT STOLLÉ (*Ber.*, 1901, 34, 3268—3269. Compare Abstr., 1896, i, 407; 1898, i, 231).—The monoalkylhydrazines are readily obtained by heating hydrazine with an aqueous solution of the corresponding alkyl sulphate; the product is freed from unaltered base by treating the mixture with benzaldehyde, and isolated in the form of its benzoyl derivative by the aid of the Schotten-Baumann reaction. The dibenzoyl derivatives of ethyl- and propyl-hydrazines may be prepared in this manner. Dibenzoylisobutylhydrazine,  $\text{N}_2\text{HBz}_2 \cdot \text{C}_4\text{H}_9$ , and dibenzoylamylhydrazine,  $\text{N}_2\text{HBz}_2 \cdot \text{C}_5\text{H}_{11}$  (from isobutylcarbinol) melt respectively at 167° and 133°. These dibenzoyl compounds dissolve in dilute sodium hydroxide solution and do not reduce ammoniacal silver nitrate or Fehling's solution even on boiling. G. T. M.

**Hydrazide and Azoimide of Phenylpropionic Acid.** By HEINRICH JORDAN (*J. pr. Chem.*, 1901, [ii], 64, 297—313).—Phenylpropionylhydrazide is obtained in quantitative yield by treatment of ethyl phenylpropionate with hydrazine hydrate; it crystallises from water in long, prismatic needles melts at 103°, and yields

a *hydrochloride*, which forms lustrous, long, prismatic needles and gives condensation compounds with benzaldehyde, salicylaldehyde, ethyl acetoacetate and acetone; these are colourless, crystalline substances melting respectively at 132.5°, 148.5°, 95°, and 93°. When treated with iodine in alcoholic solution, the hydrazide yields *s*-diphenylpropionylhydrazine, which crystallises in prismatic needles melting at 208°; this, when treated with nitrous acid, gives phenylpropionylazide, which is obtained as a light powder with a penetrating odour.

The azoimide, when boiled with ethyl alcohol, yields ethyl  $\beta$ -phenylethylcarbamate, which crystallises in small laminae, melts at 33.5°, and, when treated with water, gives diphenylethylcarbamide (m. p. 138.5°). The carbamate or the carbamide, when hydrolysed, yields  $\beta$ -phenylethylamine. The hydrobromide of the amine, which melts and decomposes at 257—259°, and compounds of the amine with mercuric chloride (m. p. 188°) and cadmium iodide (m. p. 102—103°) are described. The action of bromine on the azoimide was investigated, but only resulted in the formation of the hydrobromide of the amine.

R. H. P.

**Hydrazide and Azoimide of Phenylacetic Acid.** By ERNST BOETZELN (*J. pr. Chem.*, 1901, [ii], 64, 314—323).—The following new compounds, obtained from phenylacetic acid by methods analogous to those described in the preceding abstract, have been prepared. Phenylacetylhydrazide forms long, slender needles melting at 116°; its hydrochloride crystallises in silky needles melting and decomposing at 215°. Phenylacetylmethylenehydrazide melts at about 64°. Benzylidenephénylacetylhydrazide forms prisms melting at 154°. Salicylidene-phenylacetylhydrazide crystallises in broad prisms melting at 188°. The phenylacetylhydrazide of ethyl acetoacetate forms prisms melting at 105°. Phenylacetylazoimide forms a colourless, mobile oil with a penetrating odour, and has the properties characteristic of azoimides. The action of bromine on the azoimide yielded a colourless, crystalline substance melting at 121°. Ethyl benzylcarbamate and dibenzylcarbamide are easily obtained from the azoimide.

R. H. P.

**Hydrazide of *m*-Chlorobenzoic Acid.** By HANS FOERSTER (*J. pr. Chem.*, 1901, [ii], 64, 324—333).—Researches with *m*-chlorobenzoic acid analogous to those described in the two preceding abstracts. *m*-Chlorobenzoylhydrazide crystallises in long needles melting at 158°, and its hydrochloride in iridescent laminae decomposing at 250°. The condensation compounds of the hydrazide, with benzaldehyde, *m*-nitrobenzaldehyde, cinnamaldehyde, and acetone, are all crystalline substances, of which those from benzaldehyde and acetone melt respectively at 118° and 97°. *s*-*m*-Chlorobenzoylhydrazine crystallises in aggregates of small needles and melts at 264°. The azoimide is a colourless oil with a very penetrating odour, and easily decomposes with alcohol and water, forming ethyl *m*-chlorophenylcarbamate and *m*-dichlorodiphenylcarbamide respectively.

R. H. P.

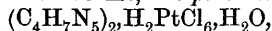
**Pyrazolone-3-acetic Acid.** By AUGUST KUFFERATH (*J. pr. Chem.*, 1901, [ii], 334—349).—Ethyl acetonedicarboxylate, when treated

with 1 mol. of hydrazine hydrate, yields *ethyl pyrazolone-3-acetate*,  $\text{NH}-\text{N} \begin{smallmatrix} \nearrow \\ \searrow \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , which crystallises from water in laminae, melts at  $189-190^\circ$ , has physiological actions similar to those of antipyrine, and forms an *acetyl* derivative, which is a microcrystalline powder melting at  $116-117^\circ$ . When treated with nitrous acid, it yields *ethyl 4-isonitrosopyrazolone-3-acetate*, which crystallises in lustrous, golden-yellow leaflets, melts at  $114-115.5^\circ$ , and forms an unstable, red *silver* salt. The silver salt, when treated with ethyl iodide, forms the corresponding *ethoxy*-derivative, which crystallises in small, yellow plates and melts at  $116-117^\circ$ . *Ethyl 4-p-azotoluene-pyrazolone-3-acetate*, obtained by the action of *p*-diazotoluene sulphate on the pyrazolone acetate, crystallises in dark-yellow needles and melts at  $172-173^\circ$ .

*Pyrazolone-3-acetylhydrazide*, obtained when ethyl acetonedicarboxylate is treated with an excess of hydrazine hydrate, is a microcrystalline powder, which melts and decomposes at  $180^\circ$ , and forms crystalline condensation compounds with benzaldehyde, salicylaldehyde, *m*-nitrobenzaldehyde, and cinnamaldehyde, melting and decomposing at  $190^\circ$ , above  $200^\circ$ , above  $145^\circ$ , and above  $145^\circ$  respectively. The *dihydrochloride* is a stable, crystalline powder which melts at  $104-105^\circ$ ; when treated with sodium nitrite, it yields *4-isonitrosopyrazolone-3-acetylazoimide*, which forms yellow crystals melting at  $97-98^\circ$ . The *azoimide*, when treated with aniline, yields *4-isonitrosopyrazolone-3-acetanilide*, which is a brown powder melting and decomposing at above  $165^\circ$ .  
R. H. P.

**Amino-derivatives of Pyrimidine.** By SIEGMUND GABRIEL (*Ber.*, 1901, 34, 3362—3366. Compare *Abstr.*, 1901, i, 168).—2:4:6-Trichloropyrimidine reacts with alcoholic ammonia under different conditions, yielding dichloroamino-, chlorodiamino-, and triamino-pyrimidines.

2:4:6-Triaminopyrimidine,  $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \nwarrow \text{N} \cdot \text{C}(\text{NH}_2) \\ \nearrow \text{N} \cdot \text{C}(\text{NH}_2) \end{smallmatrix} \text{CH}$ , is prepared by heating trichloropyrimidine or dichloroaminopyrimidine with alcoholic ammonia at  $215^\circ$ , and crystallises in short, colourless prisms, which sinter at  $242^\circ$  and melt at  $245-246^\circ$ . It is readily soluble in water, to which it imparts an alkaline reaction. The *nitrate* is sparingly soluble, the *hydrochloride*,  $\text{C}_4\text{H}_7\text{N}_5 \cdot 2\text{HCl}$ , crystallises in compact prisms or rhombohedral forms, the *platinichloride*,



forms matted, lemon-yellow needles, and the *picrate* crystallises in long needles. The base is converted by fuming nitric acid and sulphuric acid into 5-nitro-2:4:6-triaminopyrimidine,  $\text{NO}_2 \cdot \text{C}_4\text{N}_2(\text{NH}_2)_3$ , which crystallises in almost colourless, microscopic needles. The *hydrochloride* is decomposed by water, whilst the *platinichloride*, *aurichloride*, *picrate*, and *dichromate* are all crystalline. This compound is converted by reduction into tetraminopyrimidine,  $\text{C}_4\text{N}_2(\text{NH}_2)_4$ , which crystallises in flat, orange-yellow, pointed prisms, and decomposes when heated without showing a definite melting point. It is very soluble in water, forming a strongly alkaline solution. The *hydrochloride*,  $\text{C}_4\text{H}_8\text{N}_6 \cdot 3\text{HCl}$ , forms

oblong, readily soluble tablets; the *picrate* is microcrystalline, and the *platinichloride* forms stellate, yellow needles, but rapidly decomposes. A. H.

**Transformation of Dimethylketazine into 3:5:5-Trimethylpyrazoline.** By KARL WILHELM FREY and ROBERT HOFMANN (*Monatsh.*, 1901, 22, 760—776. Compare Curtius and Försterling, *Abstr.*, 1894, i, 348).—The transformation of dimethylketazine into 3:5:5-trimethylpyrazoline is not only effected by maleic acid (*loc. cit.*), but also by oxalic, succinic, tartaric, acetic, boric, metaphosphoric, and orthophosphoric acids, when these acids are either free from water or in solution in non-ionising solvents. Aqueous solutions of acids decompose, but do not transform, the ketazine. Aqueous tartaric acid partially decomposes the ketazine, but also effects some transformation. A solution of hydrogen chloride in toluene does not decompose, but transforms, the ketazine.

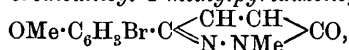
K. J. P. O.

**Pyridazines.** By OTTO POPPENBERG (*Ber.*, 1901, 34, 3257—3267. Compare Gabriel and Colman, *Abstr.*, 1899, i, 390).—*Anisoylpropionic acid*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}(\text{CH}_2)_2\cdot\text{CO}_2\text{H}$ , resulting from the condensation of anisole and succinic anhydride in the presence of aluminium chloride, crystallises from water or the ordinary organic solvents in rhombic plates melting at  $140\text{--}141^\circ$ ; it dissolves in concentrated solutions of the mineral acids to a deep red solution, the coloration being destroyed by dilution with water. The *silver* salt rapidly darkens on exposure to light.

*Anisylphenylpyridazinone*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{N} \text{---} \text{NPh} \end{smallmatrix} \text{CO}$ , produced by the action of phenylhydrazine on the alkali salts of the preceding acid, crystallises from alcohol in pale yellow, hexagonal pyramids and melts at  $105^\circ$ ; it is insoluble in water, but readily soluble in the alcohols, ethyl acetate, or glacial acetic acid, whilst it dissolves only sparingly in ether, light petroleum, or chloroform.

*Anisylpyridazinone*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{N} \text{---} \text{NH} \end{smallmatrix} \text{CO}$ , prepared by condensing anisoylpropionic acid with hydrazine hydrate in *N*-potassium hydroxide solution at the temperature of the water-bath, forms colourless, four-sided leaflets melting at  $147\text{--}148^\circ$ ; it is soluble in hot water or the ordinary organic solvents with the exception of light petroleum.

*3-Bromoanisylpyridazone*,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{C}\begin{smallmatrix} \text{CH}\cdot\text{CH} \\ \text{N} \text{---} \text{NH} \end{smallmatrix} \text{CO}$ , obtained by the action of bromine (2 mols.) on the preceding compound, is a white, crystalline product melting at  $263^\circ$ ; it is insoluble in the ordinary solvents, but dissolves, however, in solutions of the alkali hydroxides and also in glacial acetic acid. When heated with methyl iodide and sodium methoxide dissolved in methyl alcohol, the preceding pyridazone yields *3-bromoanisyl-1-methylpyridazone*,



this substance separating in white needles melting at  $153^\circ$ ; the corresponding *ethyl* derivative melts at  $140^\circ$ .

*p*-Hydroxyphenylpyridazone,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{C}\begin{smallmatrix} \text{CH}\cdot\text{CH} \\ \text{N}-\text{NH} \end{smallmatrix}\text{CO}$ , resulting from the reduction of 3-bromoanisylpyridazone with red phosphorus and hydriodic acid, forms white crystals melting at above  $290^\circ$ ; it dissolves in glacial acetic acid and in solutions of the alkali hydroxides. The benzoyl derivative,  $\text{C}_{10}\text{H}_7\text{O}_2\text{N}_2\cdot\text{COPh}$ , crystallises from alcohol in reddish leaflets melting at  $254^\circ$ .

3-Bromoanisyl-6-chloropyridazine,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{C}\begin{smallmatrix} \text{CH}\cdot\text{CH} \\ \text{N}-\text{N} \end{smallmatrix}\text{CCl}$ , produced by the action of phosphorus oxychloride on bromoanisylpyridazone, crystallises from alcohol in pale yellow needles melting at  $191^\circ$ ; when heated with sodium methoxide, it yields 3-bromoanisyl-6-methoxypyridazine melting at  $137^\circ$ , and with sodium ethoxide the corresponding ethoxy-compound melting at  $114^\circ$ . These pyridazine derivatives are all slightly basic; the chloro-compound dissolves in concentrated hydrochloric acid, but is reprecipitated by water; the methoxy- and ethoxy-bases yield *picrates* melting respectively at  $146^\circ$  and  $154^\circ$ . The chloro-base, on reduction, furnishes *p*-hydroxyphenylpyridazine (m. p.  $227^\circ$ ; compare Gabriel and Colman, *loc. cit.*); the benzoyl derivative of this product forms needles melting at  $179$ – $180^\circ$ , whilst its nitro-compound,  $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{C}_4\text{H}_3\text{N}_2$ , melts somewhat indefinitely at  $205^\circ$  and is probably a mixture of isomerides. An aminohydroxyphenylpyridazine melting at  $176^\circ$  is obtained on reducing the nitration product with red phosphorus and hydriodic acid.

3-Bromoanisyl-6-iodopyridazine, obtained as an intermediate product in the formation of *p*-hydroxyphenylpyridazine, gives rise to 3-bromoanisyl-6-methoxypyridazine. Hydroxyphenylpyridazine could not be converted into a methoxy-base, but phenylpyridazine, when treated with methyl iodide, yields the *methiodide*,  $\text{C}_6\text{H}_5\text{N}_2\text{Ph}\cdot\text{MeI}$ , crystallising in yellow needles and melting at  $179$ – $180^\circ$ .

Methylpyridazinone is prepared in theoretical yield by evaporating to dryness an aqueous solution of lævulic acid, hydrazine sulphate, and alkali hydroxide and extracting the residue with alcohol.

3-Methylpyridazone,  $\text{CMe}\begin{smallmatrix} \text{CH}\cdot\text{CH} \\ \text{N}-\text{NH} \end{smallmatrix}\text{CO}$ , results from the action of bromine on the preceding compound in glacial acetic acid solution and crystallises from water in prisms melting at  $143^\circ$ .

1:3-Dimethylpyridazone,  $\text{CMe}\begin{smallmatrix} \text{CH}\cdot\text{CH} \\ \text{N}\cdot\text{NMe} \end{smallmatrix}\text{CO}$ , obtained by methylating 3-methylpyridazone with methyl iodide and sodium methoxide, crystallises in colourless leaflets, boils at  $224^\circ$ , and melts at  $38$ – $39^\circ$ . The corresponding ethyl derivative,  $\text{C}_4\text{H}_2\text{ON}_2\text{MeEt}$ , boils at  $229$ – $231^\circ$  and is oily at the ordinary temperature.

6-Chloro-3-methylpyridazine,  $\text{CMe}\begin{smallmatrix} \text{CH}\cdot\text{CH} \\ \text{N}-\text{N} \end{smallmatrix}\text{CCl}$ , produced by treating 3-methylpyridazone with phosphorus oxychloride on the water-bath, crystallises in snow-white needles and melts at  $59^\circ$ . The chlorine atom in this compound is readily replaced by an alkoxyl group, 3-methyl-6-methoxypyridazine being formed by the action of sodium methoxide; this product is an oily base boiling at  $212$ – $215^\circ$ ; the corresponding ethoxy-compound boils at  $229$ – $231^\circ$ .

3-Methylpyridazine,  $\text{CMe} \langle \begin{smallmatrix} \text{CH}:\text{CH} \\ \text{N} \text{---} \text{N} \end{smallmatrix} \rangle \text{CH}$ , results from the reduction of 6-chloro-3-methylpyridazine with red phosphorus and hydriodic acid; it is an oil boiling at  $214.5^\circ$  under 760.5 mm. pressure and has a sp. gr. 1.0486 at  $26^\circ$ . The base yields well-crystallised, double salts with palladium, auric, platinic, and mercuric chlorides; the *picrate* crystallises in aggregates of needles and melts at  $143\text{--}144^\circ$ . 3-Methylpyridazine is miscible with water, yielding a neutral solution; it is slightly volatile in steam and readily dissolves in the ordinary organic solvents.

Methylpyridazinephthalone,  $\text{C}_4\text{H}_3\text{N}_2 \cdot \text{CH}:\text{C} \langle \begin{smallmatrix} \text{O} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \rangle \text{CO}$ , prepared by condensing 3-methylpyridazine with phthalic anhydride at  $210^\circ$ , crystallises from glacial acetic acid in dark yellow needles and melts at  $278^\circ$ .

Cinnamenylpyridazine, produced by condensing 3-methylpyridazine with benzaldehyde, is isolated in the form of its *hydrochloride*,  $\text{CHPh}:\text{CH} \cdot \text{C}_4\text{H}_3\text{N}_2 \cdot \text{HCl}$ , the yield of this product being, however, somewhat poor. The corresponding *platinichloride* decomposes on heating, whilst the *picrate*,  $\text{C}_{12}\text{H}_{10}\text{N}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3 \cdot 2\text{H}_2\text{O}$ , melts at  $199\text{--}213^\circ$ .  
G. T. M.

$\beta$ -Benzoylpicolinic Acid. By BERTHOLD JEITELES (*Monatsh.*, 1901, 22, 843—848. Compare Abstr., 1897, i, 97).—3-Phenylquinolineazone,  $\text{N-CPh}:\text{C}:\text{CH}:\text{CH} \text{---} \text{NH}:\text{CO}:\text{C}:\text{N-CH}$ , is formed when  $\beta$ -benzoylpicolinic acid, hydrazine sulphate, and potassium hydroxide are boiled together in aqueous solution; it crystallises in white scales melting and decomposing at  $236^\circ$ ; the *hydrochloride* forms yellow needles melting at  $210\text{--}211^\circ$ .

When boiled with ethyl iodide and alcoholic potash, the base yields 3-phenyl-2-ethylquinolineazone,  $\text{C}_{15}\text{H}_{13}\text{ON}_3$ , which crystallises in needles melting at  $164^\circ$ ; the corresponding *methyl* derivative forms needles melting at  $173\text{--}175^\circ$ .

Ethyl  $\beta$ -benzoylpicolinate,  $\text{C}_5\text{NH}_4\text{Bz} \cdot \text{CO}_2\text{Et}$ , prepared by heating an alcoholic solution of the acid in presence of sulphuric acid, crystallises in needles melting at  $108\text{--}109^\circ$ ; the *methyl* ester forms crystals melting at  $91^\circ$ .

On reduction of an ammoniacal solution of  $\beta$ -benzoylpicolinic acid with zinc dust,  $\beta$ -benzhydropicolinolactone,  $\text{CHPh}:\text{C}:\text{CH}:\text{CH} \text{---} \text{O-CO-C=N-CH}$ , is formed; it crystallises in needles melting at  $122^\circ$ .  
K. J. P. O.

Decomposition of Diazonium Salts by Alcohol. By ARTHUR HANTZSCH and E. JOCHEM (*Ber.*, 1901, 34, 3337—3343. Compare Spear, Abstr., 1900, i, 703; Cameron, Abstr., 1898, i, 364).—A method is described for diazotising in acetic acid solution and separating the diazo-chloride or sulphate by precipitation with ether, which gives a theoretical yield of a much purer product than that obtained by Griess' (Abstr., 1884, 1013) or Hirsch's (Abstr., 1891, 437) method.

By methyl alcohol, benzenediazonium chloride is converted completely into anisole, no benzene being produced; the actual yield of



purified anisole was 71 per cent. of the theoretical quantity. Ethyl alcohol gave a 62 per cent. yield of phenetole and a small amount of benzene. The sulphate gave, with methyl alcohol, a 69 per cent. yield of anisole, and no benzene could be isolated; with ethyl alcohol, a 58 per cent. yield of phenetole was obtained with a small amount of benzene.

*p*-Bromobenzenediazonium chloride gave, with methyl alcohol, an oil consisting chiefly of *p*-bromoanisole together with a smaller amount of bromobenzene, but with ethyl alcohol the product consisted entirely of bromobenzene.

*p*-Chlorobenzenediazonium chloride gave, with methyl alcohol, *p*-chloroanisole and a little chlorobenzene; ethyl alcohol gave an 87 per cent. yield of chlorobenzene and no chlorophenetole.

Tribromobenzenediazonium sulphate gave, with ethyl alcohol, only tribromobenzene.

T. M. L.

**Benzeneazo- $\beta$ -naphthylauramine.** By RICHARD MÖHLAU and KARL P. GRAELERT (*Ber.*, 1901, 34, 3384—3386. Compare Abstr., 1901, i, 432).—When benzeneazo- $\beta$ -naphthyl-leucauramine is heated with 7 parts of alcohol as previously described, it is converted into benzeneazonaphthylauramine, but the latter undergoes further decomposition and cannot be isolated from the solution in a state of purity. This decomposition is to a large extent avoided by taking only 1.5 parts of alcohol. The *auramine*,  $\text{NPh}\cdot\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , is then obtained in scarlet, rhombic crystals, which exhibit a bluish surface lustre and melt at 179—180°. When heated with dilute sulphuric acid, it is quantitatively converted into benzeneazo- $\beta$ -naphthylamine and tetramethyldiaminobenzophenone.

A. H.

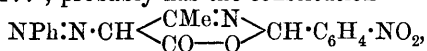
**Two New Chloroanthranilic Acids.** By PAUL COHN (*Chem. Centr.*, 1901, ii, 925; from *Mitt. Technol. Gewerb.-Mus. Wien*, 11, 178—182).—The following dyes have been prepared by the action of aromatic phenols and amines on the diazo-compounds of 4- and 6-chloroanthranilic (chloro-2-aminobenzoic) acids (Abstr., 1901, i, 637). The potassium salts of the dyes have the same colour as the solutions of the sodium salts and are easily soluble in water, except in the cases mentioned. The colours of the various dyes, when dissolved in concentrated hydrochloric or sulphuric acid or in sodium hydroxide solution, are described.

The *azo-dye* prepared from 4-chloroanthranilic acid and resorcinol is a pale red powder, melts at 108°, and is easily soluble in ether. The corresponding *dye* prepared from 6-chloroanthranilic acid is a blackish-red powder, melts at 114°, and is soluble in ether. The *dye* prepared from 4-chloroanthranilic acid and salicylic acid is an orange-red powder, melts at 132°, and is very readily soluble in ether, giving a yellow solution; the *potassium* salt is scarlet. The *dye* obtained from 6-chloroanthranilic acid and salicylic acid forms brownish-yellow scales, melts at 126°, and is easily soluble in alcohol or ether; the *potassium* salt is reddish-brown and soluble in water. The *dye* prepared from 4-chloroanthranilic acid and  $\beta$ -naphthol is a brick-red powder, melts at 94°, and is soluble in alcohol or ether; the *potassium*

salt is greenish-red with a bronze-like lustre and forms a violet solution in water. The corresponding *dye* obtained from 6-chloroanthranilic acid and  $\beta$ -naphthol is a lilac-red powder, melts at  $89-90^\circ$ , and is soluble in alcohol or ether; the *potassium* salt is violet-red and dissolves readily in water, forming a bluish-red solution. The *dye* from 4-chloroanthranilic acid and rosolic acid is a cherry-red powder, melts and decomposes at  $130^\circ$ , and forms a bluish-red solution in water, orange-yellow in alcohol; the *potassium* salt is slightly soluble in water. The corresponding *dye* obtained from the 6-acid is a brownish-red powder, melts and decomposes at  $126^\circ$ , forms a red solution in water, and is readily soluble in alcohol, giving an orange-red solution; the *potassium* salt is orange-red. The *dye* prepared from 4-chloroanthranilic acid and gallic acid is a yellowish-red powder, soluble in water or alcohol. The corresponding *dye* obtained from 6-chloroanthranilic acid is a cherry-red powder and dissolves in water, forming a cherry-red, and in alcohol, forming a pale red, solution, but is insoluble in ether.

4-Chlorosalicylic acid, prepared by boiling the diazo-compound of 4-chloroanthranilic acid, crystallises in white needles and melts at  $206-207^\circ$  (compare Varnholt, *J. pr. Chem.*, 1887, [ii], 36, 27). 6-Chlorosalicylic acid,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CO}_2\text{H}$ , obtained together with *m*-chlorophenol from the diazo-compound of 6-chloroanthranilic acid, crystallises in white needles, becomes red on exposure to the air, melts at  $166^\circ$ , is readily soluble in water and most organic solvents, is not volatile in steam, and gives a violet coloration with ferric chloride. The *ammonium* salt crystallises in brownish-yellow needles, the *potassium* salt in orange-yellow plates, and the *barium* salt in pale yellow crystals. All the preceding salts are easily soluble in water. The *silver* salt forms greyish-brown crystals and is slightly soluble in water. E. W. W.

**Fatty Aromatic Aminoazo-compounds.** By B. PRAGER (*Ber.*, 1901, 34, 3600—3606).—Ethyl  $\beta$ -aminocrotonate reacts with diazobenzene chloride in acid solution to form *ethyl benzeneazoaminocrotonate*,  $\text{NHPh}\cdot\text{N}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CMe}\cdot\text{NH}$  or  $\text{NPh}\cdot\text{N}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CMe}\cdot\text{NH}$ , which crystallises in rhomb-shaped, yellow tablets melting at  $102-103^\circ$ . When the base is boiled with water or preserved in acid solution, ammonia is eliminated and ethyl benzeneazoacetoacetate formed. *p*-Nitrobenzaldehyde converts it into a compound,  $\text{C}_{17}\text{H}_{14}\text{O}_4\text{N}_4$ , which melts at  $176-177^\circ$ , probably has the constitution



and is decomposed by acids with formation of *p*-nitrobenzaldehyde and ethyl benzeneazoacetoacetate. Ethyl  $\beta$ -methylaminocrotonate also reacts with diazobenzene and yields *ethyl benzeneazomethylaminocrotonate*,  $\text{C}_{13}\text{H}_{17}\text{O}_2\text{N}_3$ , which forms large, orange-coloured crystals melting at  $113-114^\circ$ . This substance reacts with *p*-nitrobenzaldehyde in a different manner from the foregoing compound and yields a *substance* of the formula  $\text{C}_{20}\text{H}_{22}\text{O}_5\text{N}_4$ , which melts, when quickly heated, at  $123-125^\circ$ , and on boiling with dilute acids loses methylamine, but does not yield nitrobenzaldehyde or ethyl benzeneazoacetoacetate. Ethyl diethylaminocrotonate reacts with diazobenzene chloride, yield-

ing a compound,  $C_{22}H_{29}ON_5$ , which is more stable than the foregoing aminoazo-compounds and forms yellow, rhomb-shaped plates, melting at  $135-136^\circ$ ; the *hydrochloride* melts at  $176-177^\circ$ . This substance is accompanied by ethyl benzeneazoacetoacetate, and is probably formed from 2 mols. of diazobenzene and 1 mol. of ethyl diethylaminocrotonate. The fact that ethyl diethylaminocrotonate does not yield an aminoazo-compound with diazobenzene, whilst that obtained from ethyl methylaminocrotonate reacts with *p*-nitrobenzaldehyde in a different manner from ethyl benzeneazoaminocrotonate, indicates that the last compound has the imino- and not the true amino-formula. A. H.

[Nitrated Albumins.] By OSCAR LOEW (*Ber.*, 1901, 34, 3560).—In reply to Cohnheim (*Chemie der Eiweisskörper*), it is urged that the nitrated albumins are simple derivatives of the albumins and have not undergone any complex decomposition. T. M. L.

Coagulable Components of White of Egg. By LEO LANGSTEIN (*Beitr. Chem. Physiol. Path.*, 1901, 1, 83—104).—The globulin obtained by half saturating white of egg with ammonium sulphate is probably a mixture, since it is only partially dissolved by dilute hydrochloric acid, and the soluble portion contains rather less carbon and sulphur than the original globulin. Attempts to separate globulin into components by fractional saturation with ammonium sulphate failed, however, but by treating white of egg with an equal volume of a cold saturated solution of potassium acetate, euglobulin is salted out (compare Fuld and Spiro, *Abstr.*, 1901, ii, 67). This substance contains less carbon and nitrogen than the globulin prepared by means of ammonium sulphate, gives all the reactions of albumin, and shows Molisch's reaction especially well. By the action of dilute hydrochloric acid, it yields about 11 per cent. of glucosamine. Although the quantity of euglobulin obtained is only about two-thirds of that of the globulin prepared by ammonium sulphate, ammonium sulphate does not precipitate an albumin or pseudoglobulin (Fuld and Spiro, *loc. cit.*) from the filtrate. Egg globulin cannot be classed with the mucins (compare Eichholz, *Abstr.*, 1898, i, 541).

Crystalline egg-albumin is to be regarded as a homogeneous compound, since it is precipitated by ammonium sulphate only between very narrow limits of concentration (62—68 per cent. saturation) and its composition is not affected by repeated recrystallisation. The non-crystalline albumin which is precipitated by heating the mother liquor contains rather less carbon but considerably more nitrogen and sulphur than the crystalline albumin; it corresponds with Osborne and Campbell's conalbumin (*Abstr.*, 1899, i, 837; 1900, ii, 573), and when treated with dilute hydrochloric acid yields about 9 per cent. of glucosamine. The differences in the composition of crystalline egg-albumin quoted by various investigators may be partly, but cannot be wholly, due to admixture with varying amounts of conalbumin. E. W. W.

Crystalline Albumin from the White of Crows' Eggs. By W. W. WORMS (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 448—459).—By means of 2 per cent. ammonium sulphate solution, the author has

isolated from the white of crows' eggs and crystallised an albumin which has been examined crystallographically by Larsky, who states that the crystals probably belong to the rhombic system. In 2 per cent. ammonium sulphate solution, the albumin has an  $[\alpha]_D - 29.35^\circ$ ; in aqueous solution, when freed as far as possible from ammonium sulphate by dialysis, it has an acid reaction towards litmus, which it loses on heating or on precipitation by alcohol; it gives the xanthoprotein, Adamkiewicz, and Millon colour reactions, and, when its solution is warmed with potassium hydroxide and lead acetate, it yields a precipitate of lead sulphide. Its chemical composition is: C, 52.10; H, 7.13; N, 13.76; and S, 1.075 per cent. With acids, the albumin forms compounds the rotatory powers of which are higher than those of the albumin and are further increased on heating; thus, when dissolved in 0.1 per cent. hydrochloric acid, the value of  $[\alpha]_D$  changes from  $-44.70^\circ$  to  $-58.30^\circ$  after heating; with 0.1 per cent. hydrobromic acid, the increase is from  $-36.30^\circ$  to  $-53.35^\circ$ , and with 0.5 per cent. phosphoric acid from  $-33.30^\circ$  to  $-51.25^\circ$ . The following table gives the composition of the crystalline albumins obtained by Panormoff from the whites of hens' and pigeons' eggs (Abstr., 1900, i, 126, 127, 571, 709), and of that now described by the author:

	Hen.	Pigeon.	Crow.
C .....	52.97	52.06	52.10
H .....	7.28	7.12	7.13
N .....	15.10	13.28	13.69
S .....	1.63	1.07	1.08

These numbers show the great similarity in composition between the compounds obtained from pigeons' and crows' eggs, although they are not identical, as is shown by differences in composition of the derivatives formed with hydrochloric and hydrobromic acids.

T. H. P.

**Carbohydrates of Crystallised Serum-Albumin.** By LEO LANGSTEIN (*Beitr. Chem. Physiol. Path.*, 1901, 1, 259—268).—There appear to be two carbohydrate components derivable from crystallised serum-albumin; one is glucosamine, the second is a substance which yields furfuraldehyde and an acid similar to saccharic or gulonic acid; its nature is, however, not definitely settled.

W. D. H.

**Crystalline Albumin from the Serum of Horses' Blood.** By STEPHAN MAXIMOWITSCH (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 460—469).—The author has obtained a crystalline albumin from horses' blood by the following method. The defibrinated arterial blood was mixed with an equal volume of saturated ammonium sulphate solution to separate the paraglobulin, &c. After filtering, the clear liquid was mixed with sufficient saturated aqueous ammonium sulphate to make it just turbid, and kept, when it gradually deposited a precipitate which was partly crystalline and partly amorphous and was purified by repeated recrystallisation from ammonium sulphate solution. In 2 per cent. ammonium sulphate solution, the albumin has

$[\alpha]_D + 47.47^\circ$  at  $20^\circ$ , the value for an aqueous solution being  $47.30^\circ$ . The pure, salt-free albumin has the percentage composition: C, 53.06; H, 7.05; O, 22.31; N, 15.69; S, 1.89.

The compound formed by the albumin with hydrochloric acid, the composition of which is unchanged by heating, has, in a 0.1 per cent. hydrochloric acid solution,  $[\alpha]_D 65.065^\circ$  before heating and  $72.22^\circ$  after heating. Similarly, the rotation of the hydrobromic acid compound is changed from  $[\alpha]_D 63.80^\circ$  before heating to  $69.13^\circ$  afterwards, whilst in the case of the phosphoric acid compound the values are  $62.2^\circ$  and  $67.87^\circ$  respectively. The elementary composition of the author's albumin agrees well with the formula proposed by Kuraeff for serum-albumin, namely,  $C_{225}H_{360}O_{70}N_{58}S_3$ , the percentage composition of which is: C, 53.07; H, 7.07; O, 22.01; N, 15.96, and S, 1.89. Taking this formula for the albumin prepared by the author and representing the molecule by Alb, the compounds formed with mineral acids agree well in composition with the formulæ: Alb,6HCl; 2Alb,9HBr, and Alb,4H<sub>3</sub>PO<sub>4</sub>.

T. H. P.

**Globulin as Alkali Proteid.** By L. K. WOLFF and A. SMITS (*Zeit. Biol.*, 1901, 41, 437—443).—The experiments which led Starke (*Abstr.*, 1901, i, 242) to conclude that globulins are alkali-proteids are criticised, especially those of a physico-chemical nature. W. D. H.

**Tendon Mucoid.** By W. D. CUTTER and WILLIAM J. GIES (*Amer. J. Physiol.*, 1901, 6, 155—172).—The term mucoid is adopted instead of mucin, which is reserved for gluco-proteids elaborated by secretory cells. There is more than one gluco-proteid in tendon. Analyses of five preparations of the mixed mucoids are given, the principal point of interest in which is the relatively high percentage of sulphur (2.3). The average composition and heat of combustion of the mucoids are nearly the same as those found in the mucoids separated from bone and cartilage.

W. D. H.

**Green Colouring Matter from the Blood of Animals Poisoned by Phenylhydrazine** By LOUIS LEWIN (*Compt. rend.*, 1901, 133, 599—601).—The blood of warm blooded or cold blooded animals poisoned by phenylhydrazine or its hydrochloride resembles an emulsion, and is reddish-brown by reflected light and green by transmitted light. When heated with acids, it becomes green and resembles chlorophyll. The blood contains a green, amorphous substance, *hæmoverdin*, soluble in alcohol, paraldehyde or acetone, and slightly so in ether, but insoluble in chloroform. It can be obtained, but in small quantity only, by the direct action of phenylhydrazine on defibrinated blood, and is probably a product of the alteration of hæmoglobin. It is not formed when animals are poisoned by aniline, *p*-aminophenol, diazobenzene, and hydrazine sulphate or hydrate. The spectrum of hæmoverdin shows a broad absorption band beginning at *D* and extending towards the violet, a narrow band one-third of the distance from *C* to *D*, a narrow band two-thirds of the distance from *C* to *D*, and a fourth band half-way between *D* and *E*, with considerable general absorption in the blue.

C. H. B.

**Suprarenin.** By OTTO VON FÜRTH (*Beitr. Chem. Physiol. Path.*, 1901, 1, 243—251. Compare Abstr., 1900, ii, 242).—Some further facts are added in connection with the benzoyl and other compounds of suprarenin. It is claimed that suprarenin is identical with Takamine's adrenalin.

W. D. H.

**Pentahalogen Compounds of Antimony and their Double Compounds.** By ARTHUR ROSENHEIM and WILHELM STELLMANN (*Ber.*, 1901, 34, 3377—3384).—Antimony pentachloride unites with pyridine hydrochloride to form a salt which crystallises in brownish-golden, lustrous needles and is decomposed by water. The corresponding salts with the hydrochlorides of quinoline and dimethylaniline are colourless. Double salts of antimony pentabromide (which will itself be described in a further communication) have been obtained by adding pyridine hydrobromide to the product of the action of ethereal hydrogen bromide on antimonious acid. A mixture is thus obtained of a *double* salt of antimony tribromide,  $2C_5NH_5 \cdot HBr \cdot SbBr_3$ , crystallising in yellow, lustrous needles, with a *double* salt of the pentabromide,  $2C_5NH_5 \cdot HBr \cdot SbBr_5$ , crystallising in black plates, whilst in presence of a few drops of bromine only the black crystals are formed. The corresponding salts of quinoline and dimethylaniline form yellowish-white needles.

Antimony pentachloride forms compounds with many organic oxygen derivatives, some of which are well known (Williams, this Journ., 1876, ii, 463). With acetaldehyde, it forms the *compound*,



which crystallises in druses of yellowish-white needles. The *compound* with benzaldehyde also crystallises in needles, whilst that with *acetone* forms large, very hygroscopic, prisms. With ethyl benzoate it forms a *compound*,  $SbCl_5 \cdot Ph \cdot CO_2Et$ , crystallising in lustrous, rhombic tablets; the *compound* with benzoyl chloride,  $2SbCl_5 \cdot 3COPhCl$ , crystallises in needles, the *compound* with acetamide,  $2SbCl_5 \cdot 3COMe \cdot NH_2$ , forms hygroscopic, crystalline crusts, and the *compound* with phthalic anhydride,  $2SbCl_5 \cdot 3C_6H_4 \cdot C_2O_3$ , also crystallises in extremely hygroscopic crusts. Antimony pentachloride also unites with many organic acids; with oxalic acid, it forms a *compound*,  $2SbCl_5 \cdot C_2H_2O_4$ , which crystallises in prisms. When this substance is heated with oxalic acid, the free oxalic acid is oxidised and half of the pentachloride reduced. The product of this reaction has been described by Anschütz and Evans (*Annalen*, 1887, 239, 293) as ditetrachlorostibonium oxalate. With nitrobenzene, the pentachloride yields yellow *needles* of the composition  $2SbCl_5 \cdot 3Ph \cdot NO_2$ . The pentachloride appears to react more violently when the oxygen compound contains an ethylene linking, as is the case with cinnamaldehyde. It yields no compounds with hydrocarbons, hydrogen chloride being always evolved and a chloro-derivative and antimony trichloride formed, double salts of the latter being then produced. Thus the action of the pentachloride on benzene gives rise to the *compound*  $3SbCl_5 \cdot C_6H_6$ , which crystallises in prisms; an analogous compound is formed with toluene.

A. H.

## Organic Chemistry.

**Substitution Process in the Fatty Series.** By ARTHUR MICHAEL [with W. H. GRAVES and W. W. GARNER] (*Ber.*, 1901, 34, 4028—4060).—The process of substitution in the fatty series is discussed, and recognising that the principal factors in the replacement of hydrogen by chlorine and bromine are the chemical attraction between the hydrogen atom, which is replaced, and the halogen, on the one hand, and between the halogen and carbon atoms on the other, the author considers that the presence of positive groups (methyl, &c.) renders greater the attraction between the carbon and hydrogen, whilst negative groups (carbethoxy, &c.) loosen this linking; further, positive groups attract to, and negative groups repel from, their neighbourhood negative substituents.

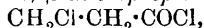
The bromination of hexane in sunlight leads mainly to the formation of  $\beta$ - and  $\gamma$ -bromohexanes, together with a small quantity of  $\alpha$ -bromohexane and a dibromohexane. By conversion of the  $\beta$ - and  $\gamma$ -bromohexanes into the corresponding hexanones (*Abstr.*, 1900, i, 321), it was shown that the quantity of the  $\beta$ -compound is considerably greater than that of the  $\gamma$ -compound.

At its boiling point, ethyl  $\alpha$ -bromobutyrate is said to be converted into ethyl  $\beta$ -bromobutyrate (Erlenmeyer and Marx). It is found, however, that after many distillations of the pure  $\alpha$ -bromo-ester, less than  $1\frac{1}{2}$  per cent. is converted into the  $\beta$ -derivative. The boiling point of pure ethyl  $\alpha$ -bromobutyrate is  $177.5^\circ$  at 764.6 mm. pressure.

$\alpha$ -Bromoisobutyric acid is not transformed into the  $\beta$ -bromo-acid at  $100^\circ$ ; the corresponding ester is only transformed to a very small extent after boiling for 2 hours.

$\alpha$ -Bromopropionic acid can be distilled under the ordinary pressure without undergoing any change; when heated for many hours at  $120$ – $130^\circ$  under pressure, a small amount of  $\beta$ -bromopropionic acid is formed. Ethyl  $\alpha$ -bromovalerate distils unchanged at  $193$ – $196^\circ$  after having been boiled.

The chlorides of several fatty acids were chlorinated by a 10 per cent. solution of chlorine in carbon tetrachloride and the resulting products fractionated under reduced pressure. Propionyl chloride yielded mainly (at least 65 per cent.)  $\beta$ -chloropropionyl chloride,



an oil boiling at  $82$ – $82.5^\circ$  (corr.) under 102 mm. pressure, together with a smaller quantity of the  $\alpha$ -chloro compound. It is noticeable that  $\alpha$ -chloropropionic acid yields some acrylic acid under the action of alkalis, whilst  $\alpha$ -bromopropionic acid gives only traces.

On chlorination of butyryl chloride,  $\beta$ -chlorobutyryl chloride forms 60 per cent. of the product, and the  $\alpha$ - and  $\gamma$ -chloro-derivatives each about 20 per cent.; at the same time, some  $\alpha\gamma$ -dichlorobutyryl chloride  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{COCl}$ , is produced as an oil boiling at  $98$ – $100$  under 42 mm. pressure, and yielding a chlorobutyrolactone when con-

verted into the corresponding acid and the latter subjected to dry distillation.

*β-Chlorobutyranilide*,  $\text{CHMeCl} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$ , prepared from aniline and *β*-chlorobutyryl chloride, crystallises in thin leaflets melting at  $89-90^\circ$ .

*iso*Butyryl chloride yields 60—70 per cent. of the *α*-chloro- and 30—40 per cent. of the *β*-chloro-derivative. *α-Chloroisobutyranilide*,  $\text{CClMe}_2 \cdot \text{CO} \cdot \text{NHPh}$ , crystallises in thin leaflets melting at  $69-70^\circ$ , and *β-chloroisobutyranilide* in leaflets melting at  $104-105^\circ$ .

From *isovaleryl chloride*, *β-chloroisovaleryl chloride* is obtained as the chief product, whilst both the *α*- and *γ*-chloro-derivatives are formed in smaller quantity.

Bromine and *isobutyryl chloride* give mainly the *α*-bromo-, together with a little of the *β*-bromo-derivative. When bromine and *isobutyryl chloride* in mol. proportion were exposed to sunlight, bright red crystals separated of a substance which melted at  $40-42^\circ$ , did not contain chlorine, and in the air readily decomposed, giving bromine and hydrogen bromide. On being dried in a desiccator over phosphoric oxide, it became white.

Two pieces of apparatus are described in the paper, which are especially adapted to the fractionation of the substances dealt with.

K. J. P. O.

**Isomerisation of Dimethylcyclopropylcarbinol.** By NICOLAI D. ZELINSKY (*Ber.*, 1901, 34, 3887—3889).—On heating cyclopropyl-dimethylcarbinol (Abstr., 1901, i, 660) with crystallised (hydrated) oxalic acid, a substance,  $\text{C}_6\text{H}_{12}\text{O}$ , was obtained as an oil with a pleasant odour, which readily distilled with steam, boiled at  $92-93^\circ$  under 746 mm. pressure, and had a sp. gr. 0.835 at  $21^\circ/4^\circ$  and  $[n]_D 1.4063$  at  $21^\circ$ . The same substance was formed when anhydrous oxalic acid was used. It

proves to be a hexylene oxide,  $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ | \quad \quad | \\ \text{CH}_2 \cdot \text{CMe}_2 \end{array} > \text{O}$ , and is probably formed by addition of the elements of water and a consequent opening of the methylene ring, followed by elimination of water with the production of the oxide.

K. J. P. O.

**Syntheses of Cyclic Tertiary Alcohols by means of Organomagnesium Compounds.** By NICOLAI D. ZELINSKY [and J. GUTT] (*Ber.*, 1901, 34, 3950—3952).—The following compounds have been obtained by Grignard's methods (Abstr., 1900, i, 382). 1:3-Dimethylcyclopentanol-3 (from 1-methylcyclopentanone-3) boils at  $88.5-89^\circ$  under a pressure of 94 mm., or at  $143-145^\circ$  under atmospheric pressure, not, however, without some decomposition; it has a sp. gr. 0.8935 at  $19^\circ/4^\circ$ ,  $n_D 1.4434$  at  $19^\circ$ , and  $\alpha 1.49^\circ$  when  $l = 0.25$  dcm. When treated with oxalic acid, it yields the unsaturated hydrocarbon,  $\begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \\ | \quad \quad | \\ \text{CH}_2-\text{CH}_2 \end{array} > \text{C} \cdot \text{CH}_2$ , which boils at  $93.5^\circ$  (corr.), has a sp. gr. 0.7734 at  $19^\circ/4^\circ$ ,  $n_D 1.4296$  at  $19^\circ$ ,  $[\alpha]_D 57.67^\circ$ , and when oxidised with potassium permanganate yields 1-methylcyclopentanone-3. 1-Methyl-3-ethylcyclopentanol-3, boils at  $71^\circ$  under a pressure of 21 mm., and has a sp. gr. 0.8974 at  $19^\circ/4^\circ$ .

R. H. P.



**Partially Acetylated Polyhydroxylic Compounds.** KNOLL & Co. (D.R.-P. 122145).—When completely acetylated hydroxylic compounds are heated with the unaltered substance, a reaction occurs between the two, resulting in the formation of a partially acetylated derivative. When triacetin and glycerol in equal proportion by weight are heated for several hours at  $200^{\circ}$ , the chief product of reaction is monoacetin. Monoacetylresorcinol results from resorcinol (2 parts) and diacetylresorcinol (3 parts) when the mixture is heated at  $170^{\circ}$ . The monoacetyl derivative of pyrogallol is produced under similar conditions from a mixture of pyrogallol and its triacetyl compound. Anthrapurpurin and its triacetyl compound yield the corresponding diacetyl derivative.

G. T. M.

**Dihydroxyisopropylhypophosphorous Acid.** By CH. MARIE (*Compt. rend.*, 1901, 133, 818—820. Compare Abstr., 1901, i, 635).—*Dihydroxyisopropylhypophosphorous acid*,  $\text{PO}_2\text{H}_3(\text{C}_3\text{H}_6\text{O})_2$ , melts at  $185$ — $186^{\circ}$  and loses acetone when heated at  $150^{\circ}$ , or when boiled with strong acids or alkalis. Mercuric chloride does not oxidise the acid in the cold, but when boiled converts it into an acid,  $\text{PO}_2\text{H}_3\text{C}_3\text{H}_6\text{O}$ ; lead oxide similarly gives the lead salt of the last-mentioned acid.

The salts of dihydroxyisopropylhypophosphorous acid are all soluble in water, and are easily prepared from the acid and the oxide or carbonate of the metal. The *sodium* salt,  $(\text{C}_3\text{H}_6\text{O})_2\text{PO}_2\text{H}_2\text{Na}\cdot 3\text{H}_2\text{O}$ , forms colourless, efflorescent crystals soluble in alcohol; the *lead* salt crystallises with  $2\text{H}_2\text{O}$ ; the *silver* salt forms anhydrous, delicate needles, sensitive to light; the *lanthanum* and *cerium* salts are anhydrous and much less soluble in hot than in cold water. The *methyl* and *ethyl* esters are prepared from the silver salt and alkyl iodide and form colourless crystals which melt respectively at  $92^{\circ}$  and  $95^{\circ}$ . A *diacetyl* derivative,  $(\text{C}_3\text{H}_6\text{O})_2\text{PO}_2\text{HAc}_2$ , melting at  $171^{\circ}$  is obtained when the acid is treated with acetic anhydride. The *dibenzoyl* derivative,  $(\text{C}_3\text{H}_6\text{O})_2\text{PO}_2\text{HBz}_2$ , was prepared by dissolving the acid in excess of pyridine and slowly adding an ethereal solution of benzoyl chloride; it melts at  $195$ — $196^{\circ}$  and is a monobasic acid. The *silver* salt,  $(\text{C}_3\text{H}_6\text{O})_2\text{PO}_2\text{AgBz}_2$ , is an insoluble, crystalline powder. The *methyl* and *ethyl* esters were obtained from the silver salt as amorphous masses.

The formula  $\text{PO}(\text{CMe}_2\cdot\text{OH})_2\cdot\text{OH}$  is suggested for the acid (compare Ville, Abstr., 1889, i, 1134).

K. J. P. O.

**Reactions of Trichloroacetic Acid.** By ARTHUR CLERMONT (*Compt. rend.*, 1901, 133, 737—738).—When mol. proportions of trichloroacetic acid, alcohol, and sulphuric acid are mixed, heat is developed and the liquid becomes opalescent. On adding water, ethyl trichloroacetate separates as an oil. Addition of its own volume of ammonia to the oil rapidly converts it into *trichloroacetamide*, which sublimates in plates resembling naphthalene, melts at  $135^{\circ}$ , and boils at  $240^{\circ}$ .

The ready formation of the ester is suggested, as a means of recognising trichloroacetic acid in the presence of other chloro-acids.

K. J. P. O.

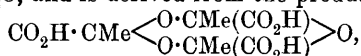
**Montan Wax.** By EDGAR VON BOYEN (*Zeit. angew. Chem.*, 1901, 14, 1110—1111).—Montan wax is a hard, crystalline wax melting at about 70° and is obtained when bitumen from brown coal is subjected to steam distillation. It appears to be a mixture of montanic acid,  $C_{29}H_{58}O_2$  (compare Hell, *Zeit. angew. Chem.*, 1900, 13, 556), and an alcohol. The alcohol is easily soluble in light petroleum, melts at 60°, and is readily attacked by sulphuric or nitric acid. The original bitumen is probably an ester of the alcohol and acid and is hydrolysed during distillation with steam.

*Potassium* and *sodium montanates* are readily soluble in hot water, but yield gelatinous precipitates on the addition of much water.

The *magnesium* salt crystallises from alcohol in needles

J. J. S.

**Transformation of Salts of Pyruvic Acid.** By A. W. K. DE JONG (*Rec. Trav. Chim.*, 1901, [ii], 20, 365—387. Compare Wolff, Abstr., 1899, i, 483).—Careful analyses of barium parapyruvate (W) (Wolff's salt) agree best with the formula  $(C_6H_6O_6Ba, 4H_2O)_n$ ; the salt is decomposed by boiling water to form the soluble *barium metapyruvate*, which, with phenylhydrazine hydrochloride, gives nearly the theoretical quantity of the phenylhydrazone of pyruvic acid. As barium parapyruvate loses exactly  $3\frac{1}{3}H_2O$  when exposed over sulphuric acid, it is probable that the salt has the molecular composition  $(C_6H_6O_6Ba)_3, 12H_2O$ , and is derived from the product



of the polymerisation of 3 mols. of pyruvic acid. The metapyruvates are possibly derived from the simpler form,  $CO_2H \cdot CMe \begin{array}{c} \diagup O \\ \diagdown O \end{array} > CMe \cdot CO_2H$ .

The barium parapyruvate, obtained by the action of dilute aqueous potassium cyanide or potassium hydroxide on barium pyruvate according to Wolff's method, is always slightly impure, containing barium carbonate and another barium salt; it does not completely dissolve on boiling with water, although the purer barium parapyruvate, obtained by transforming barium pyruvate by means of a very small quantity of barium hydroxide, readily does so. Finck's so-called basic barium salt,  $(C_9H_9O_9)_2Ba_3, Ba(OH)_2$ , is merely a mixture of the impure parapyruvate with barium carbonate and hydroxide.

A large part of the paper deals with the method of purifying barium parapyruvate and the quantitative estimation of pyruvic acid in the form of its phenylhydrazone.

W. A. D.

**Intramolecular Migration of Acyl Groups.** By WILHELM WISLICENUS and HEINRICH KÖRBER (*Ber.*, 1901, 34, 3768. Compare Abstr., 1901, i, 187).—The conversion of ethyl *O*-acetylacetoacetate into ethyl diacetoacetate at high temperatures is best carried out at 240°, but even then the yield is only 1 per cent. of the theoretical. At 260°, the yield is doubled, but a considerable amount of acetylacetone is produced. The two compounds are identified by means of their copper derivatives.

G. T. M.

**Action of certain Acid Chlorides on Methyl and Ethyl Sodioacetoacetate.** By A. BONGERT (*Compt. rend.*, 1901, 133, 820—821. Compare Abstr., 1901, i, 311).—*Ethyl propionylacetoacetate* (*C*-ester),  $\text{CMeO}\cdot\text{CH}(\text{CEtO})\cdot\text{CO}_2\text{Et}$ , formed together with the *O*-ester by the action of propionyl chloride on ethyl sodioacetoacetate, is a colourless oil boiling at  $112\text{--}113^\circ$  under 20 mm. pressure, having a sp. gr.  $1\cdot091$  at  $0^\circ/4^\circ$ , and giving a red coloration with ferric chloride; the *copper* salt crystallises in blue needles melting at  $78^\circ$ . The *O*-ester is separated from the *C*-ester by means of a saturated solution of sodium carbonate, and is a colourless oil boiling at  $121^\circ$  under 23 mm. pressure and having a sp. gr.  $1\cdot061$  at  $0^\circ/4^\circ$ ; it gives no coloration with ferric chloride. The *C*-ester represents 59 per cent. of the mixed esters.

*Ethyl C-butyrylacetoacetate*,  $\text{CMeO}\cdot\text{CH}(\text{CPr}^a\text{O})\cdot\text{CO}_2\text{Et}$ , is a colourless liquid which boils at  $112^\circ$  under 16 mm. pressure, has a sp. gr.  $1\cdot062$  at  $0^\circ/4^\circ$ , and represents 56 per cent. of the mixed esters; its *copper* salt forms blue needles melting at  $89^\circ$ . The *O*-ester boils at  $112\text{--}113^\circ$  under 10 mm. pressure and has a sp. gr.  $1\cdot033$  at  $0^\circ/4^\circ$ . With dry ammonia, the *C*-ester yields acetamide and ethyl butyrylacetate (compare Blaise, Abstr., 1901, i, 363), which boils at  $101^\circ$  under 20 mm. pressure and has a sp. gr.  $1\cdot007$  at  $0^\circ$ .

*Methyl C-isovalerylacetoacetate*,  $\text{CMeO}\cdot\text{CH}(\text{CH}_2\text{Pr}^b\text{CO})\cdot\text{CO}_2\text{Me}$ , is a colourless oil boiling at  $107\text{--}108^\circ$  under 11 mm. pressure and has a sp. gr.  $1\cdot069$  at  $0^\circ/4^\circ$ ; its *copper* salt crystallises in opalescent, blue needles melting at  $137^\circ$ . When heated with water at  $140\text{--}150^\circ$  under pressure, the ester decomposes into carbon dioxide, methyl alcohol, and isovalerylacetone,  $\text{CMeO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\text{Pr}^b$ , which is a colourless liquid with a fruity odour boiling at  $76^\circ$  under 19 mm. pressure and having a sp. gr.  $0\cdot936$  at  $0^\circ/4^\circ$ ; the *copper* salt forms small, blue crystals melting at  $142^\circ$ . With dry ammonia, the ester yields acetamide and *methyl isovalerylacetate*; the latter boils at  $95^\circ$  under 19 mm. pressure and has a sp. gr.  $1\cdot006$  at  $0^\circ/4^\circ$ ; the *copper* salt forms small, green crystals melting at  $136^\circ$ . The last-mentioned methyl ester gives, with hydrazine, 3-isobutylpyrazolone, which crystallises in white spangles melting at  $229^\circ$ . *Methyl O-isovalerylacetoacetate* is a colourless oil of disagreeable odour boiling at  $113\text{--}114^\circ$  under 11 mm. pressure, and having a sp. gr.  $1\cdot039$  at  $0^\circ/4^\circ$ .

*Methyl C-hexoylacetoacetate*,  $\text{CMeO}\cdot\text{CH}(\text{CO}\cdot[\text{CH}_2]_3\cdot\text{CH}_2\text{Me})\cdot\text{CO}_2\text{Me}$ , is a colourless liquid boiling at  $144^\circ$  under 21 mm. pressure and having a sp. gr.  $1\cdot056$  at  $0^\circ/4^\circ$ ; its *copper* salt crystallises in opalescent blue needles melting at  $92^\circ$ ; the corresponding *O*-ester boils at  $142^\circ$  under 16 mm. pressure and has a sp. gr.  $1\cdot026$  at  $0^\circ/4^\circ$ . When heated with water at  $140\text{--}150^\circ$  under pressure, the *C*-ester yields carbon dioxide, methyl alcohol, and hexoylacetone, which is a colourless oil with a fruity odour, melting at  $-18^\circ$ , boiling at  $98\text{--}100^\circ$  under 20 mm. pressure, and having a sp. gr.  $0\cdot936$  at  $0^\circ/4^\circ$ ; it is identical with the diketone obtained by Moureu and Delange (Abstr., 1901, i, 14); the *copper* salt forms small, blue, opalescent crystals melting at  $134^\circ$ .

With ammonia, methyl *C*-valerylacetoacetate gives acetamide and *methyl hexoylacetate*,  $\text{CH}_2\text{Me}\cdot[\text{CH}_2]_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ ; the latter is an

oil boiling at  $118^{\circ}$  under 19 mm. pressure and having a sp. gr. 0.991 at  $0^{\circ}/4^{\circ}$ ; with hydrazine, 3-*amylpyrazolone* is formed as white plates melting at  $195^{\circ}$ .  
K. J. P. O.

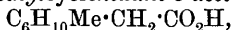
**The Red Alkali Chromo-oxalates.** By ARTHUR ROSENHEIM and ROBERT COHN (*Zeit. anorg. Chem.*, 1901, **23**, 337—341. Compare Abstr., 1896, i, 278).—Crystals of the red chromo-oxalates, obtained by treating a saturated solution of chromium hydroxide with 3 mols. of oxalic acid and 1 mol. of normal alkali oxalate, lose water at  $110^{\circ}$  and change their habit. Further heating at  $140^{\circ}$  expels no more water, but above this temperature more water is lost. The compounds contain 2 mols. of water of constitution and are dioxalatodiaquochromates,  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]\text{K}, 3\text{H}_2\text{O}$ ,  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]\text{NH}_4, 3\text{H}_2\text{O}$ ;  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]\text{Na}, 5\text{H}_2\text{O}$ . Treated with 20 per cent. ammonia (2 mols.  $\text{NH}_3$ : 1 mol. red salt), the crystals liquefy, and if the liquid be warmed until the smell of ammonia disappears, light green crystals of chromaminooxalates separate on cooling.

The silver-grey salt prepared by Wyruboff (Abstr., 1901, i, 579) contains 16 mols. of water (not 13),  $\text{Cr}_2(\text{C}_2\text{O}_4)_3, 16\text{H}_2\text{O}$ , of which 6 mols. are water of constitution. This may be a hydrate of trioxalatohexaquadichromium,  $[\text{Cr}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6], 10\text{H}_2\text{O}$ , which would be a non-ionising compound, but since a change in properties takes place on heating, it is possible that the non-ionising compound is the known non-crystallising violet chromic oxalate.  
J. McC.

**1-Methylcyclohexane-3-malonic Acid and 1-Methylcyclohexane-3-acetic Acid.** By NICOLAI D. ZELINSKY and D. ALEXANDROFF (*Ber.*, 1901, **34**, 3885—3889).—*Ethyl 1-methylcyclohexane-3-malonate*,



is formed when a mixture of ethyl malonate and 3-bromo-1-methylcyclohexane is treated with sodium; it is a colourless oil boiling at  $150\text{—}154^{\circ}$  under 10—12 mm. pressure, and has  $[\alpha]_D - 3.94^{\circ}$ . The corresponding acid,  $\text{C}_{10}\text{H}_{16}\text{O}_4$ , obtained by boiling the ester with alcoholic potassium hydroxide, forms crystals melting at  $143\text{—}144^{\circ}$ ; at the same time, a second isomeric acid,  $\text{C}_{10}\text{H}_{16}\text{O}_4$ , is formed, which crystallises in small stars melting and decomposing at  $121\text{—}122^{\circ}$ . From these facts, two stereoisomeric 1-methylcyclohexane-3-malonic acids appear to exist. On heating the acid with the melting point  $143\text{—}144^{\circ}$  at  $160^{\circ}$ , 1-methylcyclohexane-3-acetic acid,

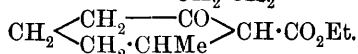


is formed as a liquid with the characteristic odour of a fatty acid, boiling at  $144^{\circ}$  under 19—20 mm. pressure and having a sp. gr. 0.9827 at  $21^{\circ}/4^{\circ}$  and  $[n]_D 1.4582$  at  $21^{\circ}$ .

*Ethyl 1:1'-di-methylcyclohexanemalonate*,  $(\text{C}_6\text{H}_{10}\text{Me}_2)_2\text{C}(\text{CO}_2\text{Et})_2$ , is formed together with the ester just described, and is a liquid boiling at  $200\text{—}205^{\circ}$  under 8—10 mm. pressure.  
K. J. P. O.

**Derivatives of  $\beta$ -Methylpimelic Acid.** By ALFRED EINHORN and LUDWIG KLAGES (*Ber.*, 1901, **34**, 3793—3798. Compare Abstr., 1897, i, 344).—Ethyl  $\beta$ -methylpimelate, when heated with sodium,

somewhat above  $100^{\circ}$ , yields the sodium salt of *ethyl methyl-2-ketohexamethylenecarboxylate*. The ester, obtained from the sodium salt, is a colourless oil, with an odour resembling that of ethyl acetoacetate, and boils at  $145\text{--}150^{\circ}$  under a pressure of 29 mm.; in alcoholic solution it gives a blue coloration with dry, a deep violet with moist, ethereal ferric chloride, and a red with aqueous ferric chloride. The ester has either the constitution  $\text{CHMe} \begin{smallmatrix} \text{CH}_2\text{---CO} \\ \text{CH}_2\text{CH}_2 \end{smallmatrix} \text{CH}\cdot\text{CO}_2\text{Et}$  or



*Ethyl methylisopropyl-2-ketohexamethylenecarboxylate*,  $\text{C}_{13}\text{H}_{22}\text{O}_3$ , prepared by the action of sodium on a mixture of isopropyl iodide and the ester just mentioned, is a colourless oil boiling at  $165\text{--}168^{\circ}$  under 20 mm. pressure. When this ester is boiled with excess of concentrated alcoholic potash, a methylisopropylketohexamethylene (b. p.  $204\text{--}206^{\circ}$ ) is formed, which is probably identical with inactive menthone (Urban and Kremers, Abstr., 1894, i, 468), as it has the same boiling point and yields an oxime with the same melting point ( $78\text{--}80^{\circ}$ ).

K. J. P. O.

**Optical Rotations of Certain Tartrates in Glycerol.** By JOHN H. LONG (*J. Amer. Chem. Soc.*, 1901, 23, 813—817).—The rotatory power of a number of tartrates in water and in glycerol at  $20^{\circ}$  has been determined with the following results:

Salt.	$[\alpha]_D$ for water.	$[\alpha]_D$ for glycerol.
$\text{KNaC}_4\text{H}_4\text{O}_6, 4\text{H}_2\text{O}$ .....	$22.1^{\circ} c=5$ to 30	$28.85^{\circ} c=5$ $28.35 c=10$ $27.87 c=15$ $27.40 c=20$ $26.96 c=25$
$\text{KSbOC}_4\text{H}_4\text{O}_6, \frac{1}{2}\text{H}_2\text{O}$ .....	$140.69 c=2$ $141.27 c=5$ $141.40 c=6$	$139.25 c=2$ $141.17 c=3$ $143.75 c=4$
$\text{K(BO)}_2\text{C}_4\text{H}_4\text{O}_6$ .....	$58.10 c=5$	$30.9 c=5$
$(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$ .....	$34.50 c=5$	$43.50 c=4$
$\text{NH}_4\text{HC}_4\text{H}_4\text{O}_6$ .....	$26.0 c=1.5$	$27.7 c=0.75$
$\text{NH}_4(\text{SbO})\text{C}_4\text{H}_4\text{O}_6, \frac{1}{2}\text{H}_2\text{O}$ ...	$150.0 c=5$	$146.10 c=3$ $146.25 c=4$
$\text{NH}_4(\text{SbO})\text{C}_4\text{H}_4\text{O}_6, 2\frac{1}{2}\text{H}_2\text{O}$ ...	$115.7 c=5$	$109.37 c=4$

These determinations show that the simple metallic tartrates examined have a higher specific rotatory power in glycerol than in water. The antimonyl tartrates have nearly the same rotation in water and glycerol, and their behaviour in general suggests a constitution different to that usually assigned to these salts. Potassium borotartrate has a lower rotatory power in glycerol than in water, probably due to the withdrawal of part or the whole of the boric radicle to form a glycerol compound.

E. G.

**Action of Ammonium Paramolybdate on the Specific Rotation of Sodium Hydrogen Tartrate.** By PETER KLASON and JOHN KÖHLER (*Ber.*, 1901, 34, 3946—3949).—The results of Itzig (Abstr.,

1901, i, 448) require correction in accordance with the researches of Klason on molybdates (Abstr., 1901, i, 162). The rule formulated by Rosenheim and Itzig (Abstr., 1900, i, 272) is wrong, as the maximum rotation given by sodium hydrogen tartrate depends, not only on the proportion of alkali ions to tartrate ions, but also on the molybdic acid, the concentration, and the temperature. R. H. P.

**Complex Derivatives of Uranic Acid.** By HERRMANN ITZIG (*Ber.*, 1901, 34, 3822—3827).—The great increase in the optical rotation of malic and tartaric acids in the presence of uranyl salts is to be attributed to the formation of complex urani-organic compounds (Walden, Abstr., 1898, ii, 149). Peligot's uranyl tartrate (*Annalen*, 1845, 56, 231, and Dittrich, Abstr., 1899, ii, 629) is not a salt, its molecular weight is normal, its dissociation factor is 0.03 per cent., and its molecular rotation lies between  $+404^\circ$  and  $410^\circ$ . The constitution suggested is  $\text{CO}_2\text{H}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{O}\cdot\text{U}\cdot\text{O}_2\cdot\text{OH}$ , *uranotartaric acid*. It forms a *potassium* salt which has only been obtained in solution and has a molecular rotation  $500^\circ$  to  $511^\circ$ ; on exposure to light, the solution rapidly turns brown: Potassium, barium, and calcium chlorides do not yield precipitates with these complex tartrates. *Uranomalic acid*,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{O}\cdot\text{U}\cdot\text{O}_2\cdot\text{OH}$ , has a molecular rotation  $-460^\circ$  to  $-467^\circ$ , and yields a *sodium* salt,  $\text{C}_4\text{H}_5\text{O}_8\text{UrNa}, 2\text{H}_2\text{O}$ , with a molecular rotation  $-682^\circ$  to  $-686^\circ$ .

J. J. S.

**Methylene Compounds of Hydroxy-acids.** By CORNELIS A. LOBRY DE BRUYN and WILLIAM ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1901, 20, 331—343).—Most of the facts of this paper have previously been dealt with (Abstr., 1901, i, 120).

The compounds previously described are better obtained by heating the hydroxy-acids with dry, powdered trioxymethylene in chloroform solution for several hours at  $150^\circ$ ; in some cases, the addition of anhydrous sodium sulphate is advantageous.

The *derivative* of *l*-tartaric acid melts at the same temperature ( $116$ — $117^\circ$ ) as that of the *d*-acid; the racemic acid *derivative*, which could not be obtained formerly, crystallises well and melts at  $103^\circ$ . Lactic, glycollic and glyceric acids yield *oily* derivatives, and saccharic acid an oil containing three formal groups and having  $[\alpha]_D + 62^\circ$  in a 4 per cent. methyl alcoholic solution; the triformal derivative of *l*-gulonic acid is an oil with  $[\alpha]_D - 48^\circ$ .

*d*-Tartaric acid, when heated for 2 hours at  $150^\circ$  with paraldehyde and sodium sulphate in chloroform, yields a small quantity (3 per cent.) of a *diacetal* derivative, which forms needles, melts at  $121^\circ$ , and has  $[\alpha]_D$  about  $+82$  in a 1 per cent. methyl alcoholic solution. Citric acid yields similarly, at  $120^\circ$ , an acetal derivative melting at  $180^\circ$ .

W. A. D.

**Bismuth Compounds derived from Organic Acids and employed in Pharmacy.** By LÉON PRUNIER (*J. Pharm. Chim.*, 1901, [iv], 14, 493—499. Compare Abstr., 1901, i, 593; ii, 106).—The crystalline compounds of bismuth with organic acids may be divided into two groups. The compounds belonging to the first group

are true bismuth salts such as bismuth salicylate, lactate, and malate and normal bismuth citrate. The second group includes those compounds which possess acid properties and form salts with potassium, sodium, and ammonium. In the latter compounds, the bismuth does not play the part of a base but rather that of an acid, so that they must be regarded as bismuthic organic acids. To this class belong bismuthiditartaric acid and the so-called basic bismuth gallate, which is really bismuthigallic acid.

H. R. LE S.

**Reduction-potential of Aldehydes.** By E. BAUR (*Ber.*, 1901, 34, 3732—3735).—The maximum value of the reduction-potential of formaldehyde (2 c.c. of 40 per cent. formalin with 50 c.c. of *N* sodium hydroxide) was found to be  $-0.343$  volt, that of acetaldehyde (2 c.c. with 50 c.c. of *N* sodium hydroxide)  $-0.238$  volt; that of benzaldehyde could not be satisfactorily measured owing to the slight solubility of the substance. The aldehydes thus act as powerful depolarisers at the anode, where they are oxidised to acids; when sodium hydroxide was electrolysed between platinum plates the current was increased more than 100-fold by adding formaldehyde in the anode compartment. The aldehydes are also capable of acting as depolarisers at the cathode by becoming reduced to alcohols, but this change proceeds only slowly and does not prevent the liberation of hydrogen.

T. M. L.

**Action of Hydrogen Chloride on Aqueous Formaldehyde.** By G. H. COOPS (*Rec. Trav. Chim.*, 1901, 20, 267—289).—Contrary to Lösekann's statement (*Chem. Zeit.*, 1890, 14, 1408), the product of this action is not chloromethyl alcohol but a mixture of this with the two substituted ethers,  $\text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\text{Cl}$  and  $\text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\text{Cl}$ ; it is not possible, as formerly stated, to separate the chloromethyl ether by simply distilling off the portion boiling below  $85^\circ$  and then washing the residue with water, and the part boiling between  $45$ — $85^\circ$  is not the ether  $\text{CH}_2\text{Cl}\cdot\text{O}\cdot\text{CH}_2\cdot\text{OH}$ .

The unpurified oily product of the action of hydrogen chloride on formaldehyde is decomposed by an excess of water giving trioxymethylene, formed by elimination of 1 HCl from  $\text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\text{Cl}$ ; cold aqueous potassium hydroxide yields only formaldehyde but on warming methyl alcohol and formic acid are produced from the latter.

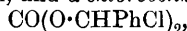
The action of alcohol on the original product develops considerable heat and gives a mixture of diethoxymethane boiling at  $86$ — $90^\circ$ , and having a sp. gr. 0.840, diethoxydimethyl ether,  $(\text{OEt}\cdot\text{CH}_2)_2\text{O}$ , which boils at  $102$ — $106^\circ$  and has a sp. gr. 0.864, and the substance,  $\text{OEt}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\text{Cl}$  which has a sp. gr. 1.02 and distils at  $47^\circ$  under 30 mm. pressure, producing considerable quantities of formaldehyde. The first two substances cannot be isolated by direct fractionation of the product of the action of alcohol, but are easily separated by treating this with potassium hydroxide or carbonate until all the chlorine is removed, washing with water, drying, and distilling. The third substance is isolated from the fraction of highest boiling point (b. p. above  $47^\circ$  under 30 mm. pressure) of the distillation of the direct product of the action of alcohol, by allowing as much of it as possible

to evaporate at the ordinary temperature under a pressure of 7—8 mm.; the residue is the nearly pure ether.

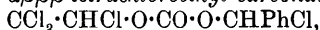
A criticism of Litterscheid's results (Abstr., 1901, i, 443) is appended. W. A. D.

**Aldehyde Derivatives containing Chlorine (Carbonylchloroaldehydes).** *FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 121223).*— $\alpha\beta\beta\beta$ -Tetrachloroethyl chlorocarbonate,  $\text{CCl}_3\cdot\text{CHCl}\cdot\text{O}\cdot\text{COCl}$ , resulting from the interaction of carbonyl chloride (1 mol.) and chloral (1 mol.) in benzene solution in the presence of dimethylaniline, is a colourless oil having a disagreeable, pungent odour and boiling at 79—80° under 16 mm. pressure. When the reaction occurs between 2 mols. of chloral and 1 mol. of carbonyl chloride or the equivalent amount of trichloromethyl chloroformate or hexachlorodimethyl carbonate also in the presence of a tertiary base, dichloralchlorocarbonyl [di- $\alpha\beta\beta\beta$ -tetrachloroethyl chlorocarbonate],  $\text{CO}(\text{O}\cdot\text{CHCl}\cdot\text{CCl}_3)_2$ , is produced and separates as a crystalline mass melting at 64° and boiling at 170° under 11 mm. pressure. This product is almost insoluble in water but readily dissolves in the ordinary organic solvents; it is tasteless, but has a slight odour of chloral.

Benzaldehyde reacts with 1 and 2 mols. of carbonyl chloride dissolved in benzene containing quinoline, giving rise to the *α-chlorobenzyl chlorocarbonate*,  $\text{CHPhCl}\cdot\text{O}\cdot\text{COCl}$ , and *α-chlorobenzyl carbonate*,



respectively; the former is an oil decomposing, when distilled under 1 mm. pressure, into benzylidene dichloride and carbon dioxide, the latter crystallises from light petroleum in rhombic prisms and melts at 105°. *α-Chlorobenzyl αβββ-tetrachloroethyl carbonate*,



obtained either by condensing chloral with *α-chlorobenzyl chlorocarbonate*, or benzaldehyde with *αβββ-tetrachloroethyl chlorocarbonate*, crystallises from light petroleum in lustrous leaflets and melts at 81.5°; it is also produced by treating a mixture of chloral and benzaldehyde with carbonyl chloride or hexachlorodimethyl carbonate in benzene containing quinoline.

These condensations all require the presence of a tertiary base, but the bases of the pyridine series are not suitable for the purpose (compare Abstr., 1901, i, 697). G. T. M.

**Nitrogen Acids.** By ANGELO ANGELI (*Atti Real. Accad. Lincei*, 1901, [v], 10, ii, 158—161).—Nitrohydroxylaminic acid,  $\text{OH}\cdot\text{N}\cdot\text{NO}_2\text{H}$ , may be regarded either as an oxidation product of hyponitrous acid,  $\text{OH}\cdot\text{N}\cdot\text{N}\cdot\text{OH}$ , or as a reduction product of nitrous acid, which, however, only in exceptional cases acts as if it had the bimolecular formula.

Besides nitrohydroxylaminic acid, both hydroxylaminesulphonic and benzenesulphonohydroxamic acids are capable of yielding the residue  $\text{:N}\cdot\text{OH}$ , so that in presence of an aldehyde they give hydroxamic acids.

The action of  $\text{:N}\cdot\text{OH}$  or an aldehyde may be one of simple addition or the residue may first combine with 1 mol. of water, forming  $\text{HN}(\text{OH})_2$ , which with the aldehyde yields the additive product  $\text{OH}\cdot\text{RCH}\cdot\text{N}(\text{OH})_2$ , this then being resolved into the hydroxamic acid



and water. In the case of aldehydes, the formation of such intermediate additive products has not been established, but in the action of the group  $\text{N}\cdot\text{OH}$  on nitrosobenzene to form nitrosophenylhydroxylamine, it is extremely probable that the product  $\text{OH}\cdot\text{NPh}\cdot\text{N}(\text{OH})_2$  is first formed. The hydrate,  $\text{NH}(\text{OH})_2$ , would correspond with hypophosphorous acid which forms well-defined additive products with aldehydes.

T. H. P.

**Researches on the Isomerisation of Pinacone and its Derivatives.** By MAURICE DELACRE (*Compt. rend.*, 1901, 133, 738—740. Compare Abstr., 1896, i, 591, 662).—Neither of the formulæ,  $\text{CMe}_3\cdot\text{COMe}$  and  $\text{O} \begin{array}{c} \text{CMe}_2 \\ | \\ \text{CMe}_2 \end{array}$ , proposed for pinacolin (methyl *tert.*butyl ketone) appear to represent completely the reactions of the compound. The author thinks that free pinacolin is a mixture of the two forms in a state of equilibrium. This view is based on the following reactions. With pinacolin, phosphorus pentachloride gives a liquid chloride,  $\text{CMe}_3\cdot\text{CCl}\cdot\text{CH}_2$ , and the solid chlorides, (a)  $\text{CMe}_3\cdot\text{CMeCl}_2$ , from which an acetylene hydrocarbon is obtainable; (b)  $\text{CMe}_3\cdot\text{CCl}_2\cdot\text{CH}_2\text{Cl}$ , which is formed by the action of phosphorus pentachloride on the liquid chloride; (c)  $\text{CClMe}_2\cdot\text{CClMe}_2(?)$ , which yields, with alcoholic potassium hydroxide, tetramethylethylene. With moist pinacolin, sodium gives symmetrical reduction products.

Pinacolyl alcohol yields a bromide which is identical with the compound obtained from hydrogen bromide and tetramethylethylene. The liquid chloride above mentioned yields on reduction a hydrocarbon,  $\text{CMe}_3\cdot\text{CH}\cdot\text{CH}_2$ , boiling at  $44^\circ$ , which, with hydrogen bromide, forms an additive product isomeric with pinacolyl bromide; it reacts with moist silver oxide, producing mainly a secondary alcohol,



whilst with dilute potassium hydroxide, tetramethylethylene is formed. Pinacolyl bromide, on the other hand, with any moist oxide, gives, at  $80$ — $100^\circ$ , mainly tetramethylethylene, together with a small quantity of the secondary alcohol.

Oxidation of pinacolin yields 50 to 60 per cent. of trimethylacetic acid and acetone (?).

The hydrocarbon to which Couturier (Abstr., 1893, i, 244) ascribes the formula  $\text{CMe}_3\cdot\text{CH}\cdot\text{CH}_2$ , is regarded by the author as having the formula  $\text{CMe}_2\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}_2$ , as the chloride formed from it and hydrogen chloride is identical with pinacolyl chloride.

The formula  $\text{OH}\cdot\text{CMe}_2\cdot\text{CMe}\cdot\text{CH}_2$  is given to the compound formed in the action of potassium hydroxide on the additive product of hypochlorous acid and tetramethylethylene.

K. J. P. O.

**Terpenes and Ethereal Oils.** By OTTO WALLACH (*Annalen*, 1901, 319, 77—120).—[With AD. GILBERT.]—The base,  $\text{C}_8\text{H}_{13}\text{N}$ , produced by treating methylheptenoneoxime with phosphoric oxide (compare Abstr., 1900, i, 46), may contain either a pyridine or a pyrroline nucleus, and accordingly the base,  $\text{C}_8\text{H}_{17}\text{N}$ , obtained by reducing this tertiary amine with sodium and alcohol, is either a trimethylpyridine,

$\text{CMe}_2 \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{CHMe} \end{array} \text{CH}_2$ , or  $\text{CMe}_2 \begin{array}{c} \text{CH}_3 - \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CHMe} \cdot \text{NH} \end{array} \text{CH}_2$ , or a trimethyl-  
 pyrrolidine,  $\text{CHMe}_2 \cdot \text{CH} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{NH} - \text{CHMe} \end{array}$ , or  $\text{CHMe}_2 \cdot \text{CH} \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ | \\ \text{CHMe} \cdot \text{NH} \end{array}$ .

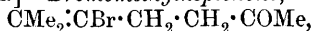
The physical properties of the new base favour the view that it is a piperidine derivative. It is a colourless oil, having an odour like that of piperidine and boiling at  $166^\circ$ ; the sp. gr. is 0.859 at  $19^\circ$  and  $n_D$  1.4596. The hydrochloride is syrupy, the *platinichloride* crystallises in needles melting at  $173^\circ$ , the *aurichloride* melts at  $118^\circ$ . The new base is a secondary amine isomeric with coniine. With nitrous acid, it yields an oily *nitrosoamine* boiling at  $134^\circ$  under 18 mm. pressure, and when converted into the cyanamide,  $\text{C}_8\text{H}_{16}\text{N}\cdot\text{CN}$ , it gives rise to two *thiocarbamides* by the action of ammonium sulphide (compare Abstr., 1899, i, 658), one forming plates melting at  $171^\circ$ , the other crystallising in woolly needles and melting at  $154\text{--}155^\circ$ . When treated with excess of methyl iodide in methyl alcohol, the amine gives rise to two *quaternary iodides*,  $\text{C}_8\text{H}_{16}\text{NMe}_2\text{I}$ , which are separated by the difference of their solubilities in alcohol. The  $\alpha$ -compound is only slightly soluble in alcohol or water, and melts at  $238^\circ$ ; the corresponding *aurichloride*,  $\text{C}_8\text{H}_{16}\text{NMe}_2\text{AuCl}_4$ , melts at  $105^\circ$ . The  $\beta$ -compound, produced in larger amount, crystallises in needles and melts at  $159\text{--}160^\circ$ ; it is readily soluble in water or alcohol; the corresponding *aurichloride* melts at  $99^\circ$ . These quaternary iodides yield isomeric tertiary bases when their hydroxides are distilled in a vacuum.

The tertiary *amine*,  $\text{C}_8\text{H}_{15}\cdot\text{NMe}$ , derived from the  $\alpha$ -iodide boils at  $167\text{--}169^\circ$  and yields a quaternary *iodide*, crystallising in lustrous scales and melting at  $231^\circ$ .

The isomeric tertiary *amine* produced from the  $\beta$ -iodide boils at  $171\text{--}173^\circ$ . The quaternary *iodide* prepared from this base is not homogeneous, and is obtained as a mixture of plates melting at  $217^\circ$ , and needles melting at  $201^\circ$ .

The iodides of the tertiary bases yield hydroxides, which, on distillation in a vacuum, give rise to a mixture of trimethylamine and unsaturated hydrocarbon. The *hydrocarbon*,  $\text{C}_8\text{H}_{14}$ , from the  $\beta$ -compound, boils at  $107\text{--}110^\circ$  and is isomeric with conylene.

[With A. BLEMBEL.]—*Bromomethylheptenone*,



produced by adding bromine to a methyl alcohol solution of methylheptenoneoxime and pouring the mixture into a 10 per cent. solution of sodium hydroxide, is isolated in the form of its *semicarbazone*,  $\text{C}_8\text{H}_{13}\text{Br}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , a substance crystallising from alcohol in white leaflets and melting at  $184^\circ$ . The ketone itself, obtained from the semicarbazone by hydrolysis with 50 per cent. sulphuric acid, boils at  $96^\circ$  under 9 mm. pressure, and has a sp. gr. 1.2715 at  $20^\circ$  and  $n_D$  1.4913. The *oxime*,  $\text{C}_8\text{H}_{13}\text{Br}\cdot\text{NOH}$ , melts at  $58^\circ$  and boils at  $140^\circ$  under 9 mm. pressure; it is exceedingly soluble in the ordinary organic solvents. The *benzylidene* compound,  $\text{C}_8\text{H}_{11}\text{OBr}\cdot\text{CHPh}$ , formed from its generators, dissolved in alcohol containing a small amount of sodium hydroxide, crystallises in lustrous, white leaflets and melts at  $155^\circ$ .

The bromo-ketone, when treated with sodium hypobromite, yields  $\gamma$ -bromo- $\delta$ -methyl- $\gamma$ -hexenoic acid,  $\text{CMe}_2\cdot\text{CBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , and this substance, on treatment with bromine, gives  $\gamma\gamma\delta$ -tribromo- $\delta$ -methylhexoic acid,  $\text{CMe}_2\text{Br}\cdot\text{CBr}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , which separates from alcohol in crystals melting at  $161^\circ$ .

The bromo-ketone is reduced to methylheptenone by sodium and alcohol, whilst the oxime, under these conditions, yields methylheptenylamine.

Lævulic acid is obtained by oxidising the bromo-ketone, first with potassium permanganate, and then with chromic acid.

The semicarbazone, or a solution of its generators, when heated for some time with dilute sulphuric acid, yields a mixture containing two bases, one having the formula  $\text{C}_8\text{H}_{11}\text{N}$ , which is identified as 4-amino-1:3-xylene, whilst the other, having the composition expressed by  $\text{C}_8\text{H}_{14}\text{N}_2$ , is probably a hydrazine derivative; the latter base boils at  $175^\circ$  under 15 mm. pressure and evolves ammonia when distilled under the ordinary pressure. These bases are also formed on boiling the bromo-ketone with hydrazine sulphate. The production of the xyldine base is evidence in favour of the constitution indicated for the bromomethylheptenone.

[With HEINRICH MEYER and E. MITTELSTENSCHIED.]—The unsaturated base,  $\text{C}_8\text{H}_{15}\text{N}$ , obtained by adding bromine to methylheptenylamine hydrochloride, evaporating down the aqueous solution of the additive compound and setting free the amine with an alkali hydrate, possesses many exceptional properties. It forms, with benzaldehyde, an additive compound having the composition  $\text{C}_{15}\text{H}_{21}\text{ON}$  and melting at  $99$ – $100^\circ$ .

The compound,  $\text{C}_{15}\text{H}_{22}\text{O}_2\text{N}$ , produced by the Schotten-Baumann reaction, is a benzoyl derivative of the unsaturated base, *plus* the elements of a mol. of water.

The base,  $\text{C}_8\text{H}_{14}\text{NMe}$ , obtained in the form of its iodide by mixing together methyl iodide and the unsaturated amine at  $0^\circ$ , boils at  $164$ – $166^\circ$  and has a sp. gr. 0.852,  $n_D$  1.4663 at  $20^\circ$ , mol. refraction 45.21 (calculated 45.08). The iodide crystallises from alcohol and ether in colourless needles melting at  $200$ – $205^\circ$ ; the *picrate* and *platinichloride* melt respectively at  $84$ – $85^\circ$  and  $194$ – $195^\circ$ . The monomethyl derivative is not acted on by nitrous acid and therefore seems to be a tertiary base.

Further methylation of the tertiary amine and treatment of the product with moist silver oxide results in the formation of trimethylamine and a ketone,  $\text{C}_8\text{H}_{14}\text{O}$ .

This ketone, a new *methylheptenone*, is more readily prepared by treating the unsaturated base,  $\text{C}_8\text{H}_{15}\text{N}$ , with nitrous acid; it boils at  $161$ – $162^\circ$ , and has a sp. gr. 0.842 and  $n_D$  1.43096 at  $20^\circ$ , the found and calculated values for the mol. refraction being 38.73 and 38.72 respectively. Its *semicarbazone* melts at  $93$ – $95^\circ$ , and its *oxime* boils at  $99^\circ$  under 12 mm. pressure.

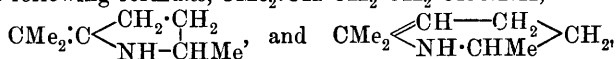
*Methylheptenol*,  $\text{C}_8\text{H}_{15}\cdot\text{OH}$ , produced by reducing the new ketone with sodium and moist ether, boils at  $166$ – $167^\circ$ ; it is accompanied by a syrupy product of high boiling point, which is probably a pinacone.

This alcohol differs from that obtained from natural methylheptenone in being unaffected by boiling dilute sulphuric acid.

*Methylheptenylamine*,  $C_8H_{15}\cdot NH_2$ , produced from the preceding oxime, boils at  $156-158^\circ$ ; its *oxalate*, *hydrochloride*, *platinichloride*, and *carbamide* melt at  $153-154^\circ$ ,  $207-209^\circ$ ,  $146-147^\circ$ , and  $123^\circ$  respectively.

The new methylheptenone, on oxidation with potassium permanganate and chromic acid, yields a mixture of *isobutyric* and *oxalic* acids.

The following formulæ,  $CMe_2\cdot CH\cdot CH_2\cdot CMe\cdot NH$ ,



are discussed in connection with the unsaturated base,  $C_8H_{15}N$ .

A ketone formed from a base having the second formula would have a constitution corresponding with  $CHMe\cdot CH\cdot CH_2\cdot CO\cdot CHMe_2$ , and this substance would, on oxidation, yield *isobutyric* acid.

Further investigations, however, are required in order to explain fully the constitutions of the compounds described in the last section of this communication.

G. T. M.

**Condensation Reactions of Diketones.** By THEODOR POSNER (*Ber.*, 1901, **34**, 3973—3986. Compare *Abstr.*, 1901, i, 14 and 703).— $\alpha$ -Diketones can react with 2 mols. of hydroxylamine, phenylhydrazine, or semicarbazide, and different substituents do not hinder the condensation, as is the case with mercaptans.  $\beta$ -Diketones react with semicarbazide (1 mol.), yielding pyrazole derivatives.

*Diacetyl disemicarbazone*,  $C_2Me_2(N\cdot NH\cdot CO\cdot NH_2)_2$ , crystallises from acetic acid in small plates melting at  $278-279^\circ$  and is insoluble in most solvents. *Diacetyl phenylhydrazone-semicarbazone*,

$N_2HPh\cdot CMe\cdot CMe\cdot N\cdot NH\cdot CO\cdot NH_2$ , crystallises in yellow needles melting at  $229-230^\circ$  and is insoluble in water or ether.

*Acetylpropionyl disemicarbazone*,

$NH_2\cdot CO\cdot N_2H\cdot CMe\cdot CEt\cdot N_2H\cdot CO\cdot NH_2$ , crystallises in needles melting at  $251-252^\circ$ ; attempts to prepare the monosemicarbazone were unsuccessful.

The *phenylhydrazone-semicarbazone*,  $N_2HPh\cdot CMe\cdot CEt\cdot N_2H\cdot CO\cdot NH_2$ , melts at  $199-200^\circ$ .

Benzil and semicarbazide react only when their alcoholic solution is warmed, and the product is a mixture of  $\alpha$ -benzilmonosemicarbazone, crystallising in yellow needles and melting at  $164-165^\circ$  with the stereoisomeric  $\beta$ -compound melting at  $221^\circ$ ; when the mixture is heated for several hours, the  $\beta$ -isomeride only is formed, but when warmed at  $60^\circ$  for half-an-hour, the  $\alpha$ -compound is the chief product.

3:5-Dimethylpyrazole-1-carboxylamide,  $\begin{matrix} CH=CM \\ CMe=N \end{matrix} > N\cdot CO\cdot NH_2$ , is

obtained by the action of an aqueous solution of semicarbazide hydrochloride, and sodium acetate on an alcoholic solution of acetylacetone. It sinters at  $109^\circ$ , is completely melted at  $111.4-112.4^\circ$ , and dissolves in hot water, alcohol, or ether. On treatment with ammoniacal silver

nitrate, it yields the silver derivative of 3 : 5-dimethylpyrazole (Rothenburg, Abstr., 1894, i, 384).

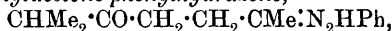
3 : 4 : 5-Trimethylpyrazole-1-carboxylamide, obtained from methylacetylacetone, crystallises in needles melting at 148—149°, and on treatment with ammoniacal silver nitrate yields the silver derivative of 3 : 4 : 5-trimethylpyrazole. Methylacetylacetone and phenylhydrazine acetate yield 1-phenyl-3 : 4 : 5-trimethylpyrazole,  $\begin{array}{c} \text{CMe} \cdot \text{CMe} \\ \parallel \quad \parallel \\ \text{N} - \text{NPh} \end{array} > \text{CMe}$ ,

in the form of an oil boiling at 278—280° under 768 mm. pressure; the hydrochloride melts at 52—53°, and the picrate at 100—103°.

3-Phenyl-5-methylpyrazole-1-carboxylamide, obtained from benzoylacetone and semicarbazide, crystallises in small needles melting at 154—156°. Benzoylacetophenone and semicarbazide react only slowly and require vigorous boiling in aqueous alcoholic solution for 4 hours. The product is Knorr and Duden's 3 : 5-diphenylpyrazole (Abstr., 1893, i, 231). Benzoylacetophenone and hydroxylamine yield diphenylisooxazole (Abstr., 1896, i, 189).

Acetylacetonedisemicarbazone,  $\text{C}_2\text{H}_4(\text{CMe} \cdot \text{N}_2\text{H} \cdot \text{CO} \cdot \text{NH}_2)_2$ , melts at 223—224° and is insoluble in most solvents with the exception of boiling water.

Dimethylacetonylacetone-phenylhydrazone,



crystallises in brownish-red needles melting at 55—57°; the corresponding semicarbazone,  $\text{CHMe}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{N}_2\text{H} \cdot \text{CO} \cdot \text{NH}_2$ , melts at 201°. The diphenylhydrazone and disemicarbazone could not be obtained. J. J. S.

**Carbamide Derivatives of Sugars. II.** By N. SCHOORL (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 4, 214—217).—A detailed account of the physical and chemical properties of dextrose-ureide previously described (Abstr., 1901, i, 258). It has a sp. gr. 1.48 at 25° and the heat of combustion is 8307 *K* per gram-molecule. The ureide does not reduce a slightly acid solution of copper acetate, is only slowly oxidised at the ordinary temperature by hypobromites, but is quickly decomposed by nitrous acid at 0°. Its aqueous solution is only slightly hydrolysed by alkalis, but the rotatory power undergoes a rapid change. When acetylated in the presence of zinc chloride, the ureide yields a crystalline *pentacetyl* derivative melting at 200°, and, when benzoylated, a *tetrabenzoyl* derivative melting at 117°. The following substituted carbamides have been found to change the rotation of a solution of dextrose in dilute sulphuric acid: methyl-, phenyl-, and benzyl-carbamides, *as*-dimethylcarbamide, thiocarbamide, biuret, and urethane.

The only sugars which condense with carbamide are those which contain an open carbonyl group, such as the aldopentoses and aldohexoses and of the bihexoses, lactose and maltose. R. H. P.

**Optical Rotatory Power of Sucrose dissolved in Pyridine.** By GUY MAURICE WILCOX (*J. Physical Chem.*, 1901, 5, 587—599).—The specific rotation of sucrose in pyridine solution at 25° decreases from 86.7 for a 1 per cent. solution to 83.6 for a 6.25 per cent. solu-

tion, the curve being approximately a straight line. Substitution of water for pyridine causes a considerable decrease in the rotation and a minimum value of 66.0 was obtained when the percentage of water reached 80, the value in pure water being 66.6. The effect of temperature was investigated between  $-10^{\circ}$  and  $105^{\circ}$ ; the specific rotation decreased from 88.7 to 77.0 between these limits, the rate of increase being slightly greater at low than at high temperatures, whilst the temperature coefficient is throughout considerably greater than in aqueous solution, a result probably due to the greater expansion of the pyridine. The molecular weight as determined by the boiling point gave results lower than the theoretical and increasing with concentration.

L. M. J.

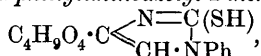
**Inversion of Sucrose.** By EDMUND O. VON LIPPMANN (*Ber.*, 1901, 34, 3747—3750).—A criticism of recent theories of sugar inversion (compare Abstr., 1901, ii, 89).

T. M. L.

**Detection of Chitosamine [Glucosamine].** By CARL NEUBERG and H. WOLFF (*Ber.*, 1901, 34, 3840—3846).—*Glucosamine hydrochloride p-nitrophenylhydrazone*,

$\text{OH}\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{OH}]_3\cdot\text{CH}(\text{NH}_2, \text{HCl})\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , forms microscopic needles melting and decomposing at  $210^{\circ}$  and dissolves in water, yielding a pale yellow solution which turns deep red on the addition of fixed alkalis. The corresponding *hydrobromide* begins to decompose at  $190^{\circ}$ .

*4-Tetrahydroxybutyl-1-phenyliminoazoly-2-mercaptan*,



obtained from glucosamine and phenylthiocarbimide, forms long, colourless prisms melting at  $208^{\circ}$  and has  $[\alpha]_D + 58.20'$ ; it yields precipitates with silver nitrate, copper sulphate, or mercuric chloride solution. The corresponding *1-allyl* derivative melts at  $138^{\circ}$ .

None of the compounds described above is of use in the identification of glucosamine, as, although readily obtained from the pure base, they cannot be obtained in a crystalline form from mixtures containing other bases. The best method of identification is the conversion into norisoscacharic acid (Fischer and Tiemann, Abstr., 1894, i, 167), the alkaloidal salts of which are characteristic. The *cinchonine* salt of this acid crystallises in elastic needles containing  $2\text{H}_2\text{O}$  and melting at  $208^{\circ}$ , it is soluble in hot water, but only sparingly so in cold, is insoluble in acetone, chloroform, ethyl acetate, or benzene, and has  $[\alpha]_D - 175^{\circ}$ . The *quinine* salt melts at  $207^{\circ}$  and has  $[\alpha]_D - 125^{\circ}$  and the *brucine* salt melts at  $199^{\circ}$ .

J. J. S.

**Ethylenediamine Carbonate.** CHEMISCHE FABRIK AUF ACTIEN (E. SCHERING) (D.R.-P. 123138).—The substance,  $\begin{matrix} \text{CH}_2\cdot\text{NH}_2\cdot\text{O} \\ \text{CH}_2\text{—NH} \end{matrix} > \text{CO}$ ,

obtained by passing carbon dioxide into a cooled and stirred solution of ethylenediamine, is a crystalline substance vaporising at  $170^{\circ}$ ; it is stable on exposure, its solution has an alkaline reaction and taste, and when evaporated leaves a syrupy residue.

G. T. M.

**Discrimination between Basic and Acidic Functions in Solutions of Amino-acids by means of Formaldehyde.** By HUGO SCHIFF (*Annalen*, 1901, 319, 59—76. Compare Abstr., 1899, i, 870).—Glycine is appreciably acid to phenolphthalein, but requires only about half the calculated amount of potassium hydroxide to produce neutrality; in the presence of formaldehyde, however, it behaves as a monobasic acid, but even in this case the quantity of alkali required diminishes as the solution is diluted. Phenylglycine, owing to the acidic character of the phenyl group, behaves in solution as a monobasic acid, even without the addition of formaldehyde; the three aminobenzoic acids exhibit a similar behaviour.

$\alpha$ -Alanine itself is only feebly acid towards phenolphthalein, and even in a concentrated solution of formaldehyde it requires less than 1 mol. of potassium hydroxide to give the neutral reaction.

*Methylene- $\alpha$ -alanine*, a white, amorphous, soluble substance, behaves as a monobasic acid in concentrated solutions; it yields the *copper* salt,  $(\text{CH}_2 \cdot \text{N} \cdot \text{C}_2\text{H}_4 \cdot \text{CO}_2)_2\text{Cu} \cdot 2\text{H}_2\text{O}$ . Taurine is slightly acid in concentrated, and neutral in dilute, solutions, but behaves as a monobasic acid in the presence of the aldehyde, even when the dilution is considerable.

Leucine and tyrosine in strong solutions of the aldehyde behave as monobasic acids, but the action of this reagent is rendered incomplete on dilution. Methyleneasparagine reacts as a monobasic acid. Aspartic acid does not yield a methylene compound nor is its basicity appreciably affected by the aldehyde. Its sodium salt, however, becomes distinctly acid when treated with formaldehyde, the amount of potassium hydroxide required to neutralise the second carboxyl group being 75—80 per cent. of the theoretical; the action of the aldehyde diminishes rapidly as the solution is diluted.

Since neutral asparagine is changed into monobasic aspartic acid by the conversion of the radicle  $-\text{CO} \cdot \text{NH}_2$  into carboxyl, it follows that the sodium salt is  $\text{CO}_2\text{H} \cdot \text{CH}(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Na}$ , the acid function of the second carboxyl being neutralised by the adjacent amino-group.

Tetraspartic acid itself is tetrabasic, but the fifth carboxyl group is indicated under the influence of the aldehyde, 4.8 mols. of potassium hydroxide being required to neutralise 1 mol. of the acid in the presence of this reagent.

These changes in basicity are reversible and are affected by the mass of the reagents, the results obtained varying with the relative proportions of formaldehyde and water.

On adding formaldehyde to aqueous solutions of ammonium salts, neutral hexamethylenetetramine is produced, and the combined acid set free can be titrated with standard alkali solutions. On the other hand, formaldehyde can be estimated alkalimetrically by adding to its solution excess of ammonium chloride. Boric acid and other weak acids are readily liberated from their ammonium salts by treating these compounds with formaldehyde solution. G. T. M.

**Resolution of Racemic Amino acids. V.** By EMIL FISCHER and RUDOLF HAGENBACH (*Ber.*, 1901, 34, 3764—3767. Compare Abstr., 1900, i, 172, 646, 647).—1-Benzoyl-d-amino-n-hexoic acid,

$C_{13}H_{17}O_3N$ , isolated from the racemic acid by means of the cinchonine salt, crystallises from hot water in long, colourless needles with  $\frac{1}{2}H_2O$ , melts at  $53^\circ$  (corr.), and has  $[\alpha]_D - 21.9^\circ$  in water at  $20^\circ$ . The *l*-aminohezoic acid prepared from this has  $[\alpha]_D - 22.4^\circ$ ; Schulze and Likiernik obtained by fermentation an acid which had  $[\alpha]_D - 26.5^\circ$  (Abstr., 1893, i, 309).

*d*-Benzoyl- $\alpha$ -amino-*n*-hezoic acid has  $[\alpha]_D + 21.4^\circ$ . *d*-Aminohezoic acid has  $[\alpha]_D + 21.3^\circ$ .  
T. M. L.

**Derivatives of the Alkali Metals and Cyclic Aminoketones.** By EMANUEL MERCK (D.R.-P. 121505. Compare Abstr., 1901, i, 670).—Tropinone, vinylldiacetoneamine, and triacetoneamine, when dissolved in dry ether and treated with sodium ethoxide or methoxide, either solid or dissolved in absolute alcohol, yield yellowish-white precipitates consisting of the respective sodium derivatives. The potassium derivatives are produced from potassium ethoxide in a similar manner.  
G. T. M.

**Formation of Carbamide by the Oxidation of Physiological Nitrogenous Substances by means of Permanganate in Acid Solution.** By ADOLF JOLLES (*Ber.*, 1901, 34, 3786—3787).—In opposition to Falta (Abstr., 1901, i, 795), the author finds that uric acid in a 0.02 per cent. aqueous solution containing 1 per cent. of sulphuric acid gives a quantitative yield of carbamide, but not the slightest trace of ammonia when oxidised with a slight excess of permanganate added gradually to the boiling solution.  
G. T. M.

**Crystallography of some Derivatives of Carbamide.** By G. MEZ (*Zeit. Kryst. Min.*, 1901, 35, 242—271).—The results are given of detailed determinations of the crystallographic and other physical characters of carbamide and of sixteen of its derivatives. The relations between the angular elements and between the topic axial ratios, depending on the introduction of different radicles, are discussed.  
L. J. S.

**Primary Arsines.** By ARTHUR W. PALMER and WILLIAM M. DEHN (*Ber.*, 1901, 34, 3594—3599).—*Methylarsine*,  $AsH_2Me$ , is formed by the reduction of methylchloroarsine,  $AsMeCl_2$ , but is best prepared by acting on an alcoholic suspension of sodium methylarsenate and amalgamated zinc dust with hydrochloric acid in an atmosphere of dry hydrogen in an apparatus entirely made of glass. The gas evolved is passed through water, dried over soda-lime, and liquefied by solid carbon dioxide. It is a colourless, readily mobile liquid which boils at  $2^\circ$  under 755 mm. pressure, and at  $17^\circ$  under 1.5 atmospheres pressure. It has the penetrating, repulsive odour of cacodyl and fumes in the air, but is not spontaneously inflammable. If air has access to the apparatus in which it is prepared, the arsine is oxidised to a lustrous, red substance, the nature of which is not known. When pure, dry oxygen is added to gaseous methylarsine over mercury, equal volumes of the two gases combine, forming water and methylarsine oxide,  $AsMeO$ , which then slowly combines with oxygen forming methylarsenic acid.



On one occasion, the addition of the oxygen was followed by a mild explosion, and the whole of the arsenic was deposited in the free state. The arsine is oxidised by concentrated nitric acid to arsenious acid and monomethylarsinic acid, and when passed into an alcoholic solution of iodine yields arsinmethyl iodide.

*Monophenylarsine*,  $\text{AsH}_2\text{Ph}$ , is prepared by a similar reaction from calcium monophenylarsenate, although La Coste and Michaelis were unable to obtain it in this way (*Annalen*, 201, 203, 209). It is a transparent, strongly refractive oil, which boils at  $148^\circ$ , and smells, when concentrated, like phenylcarbamine, when dilute, like hyacinths. In the air, it is converted into a yellow substance, which melts at  $195\text{--}208^\circ$  and is probably arsenobenzene. Nitric acid converts the arsine into monophenylarsinic acid and a yellow oil of unknown nature. A. H.

**Simultaneous Formation of Isomeric Substitution Derivatives of Benzene. VI. Nitration of Iodobenzene.** By ARNOLD F. HOLLEMAN and B. R. DE BRUYN (*Rec. Trav. Chim.*, 1901, [ii], 20, 352—359. Compare Abstr., 1900, i, 387, 638; 1901, i, 318).—The proportion of *o*- and *p*-iodonitrobenzenes in the product of nitration of iodobenzene was determined by the method of melting points and of sp. gr. (*loc. cit.*). The product obtained by adding gradually 25 grams of iodobenzene to a mixture of 50 c.c. of nitric acid of sp. gr. 1.48 with 10 c.c. of acid of sp. gr. 1.52 consists at  $-30^\circ$  of 35.3 per cent. of *o*- and 64.7 per cent. of *p*-iodonitrobenzene, and at  $0^\circ$  of 34.2 per cent. of *o*- and 67.8 of *p*-compound.

Pure *o*-iodonitrobenzene, obtained from pure *o*-nitroaniline, has a sp. gr. 1.8100 at  $155^\circ/4^\circ$  and melts at  $54^\circ$ ; it is difficult to purify the *o*-compound obtained by the nitration of iodobenzene, and Körner, in giving the melting point as  $49.4^\circ$ , had not obtained the pure substance. *m*- and *p*-Iodonitrobenzenes have respectively sp. grs. 1.8039 and 1.8090 at  $155^\circ/4^\circ$ .

The eutectic point of a mixture of *o*- and *p*-iodonitrobenzenes is  $45.2^\circ$ ; the product of nitration at  $30^\circ$  gave a value for this constant of  $43.5^\circ$ , and at  $0^\circ$  a value  $43.1^\circ$ . The depression is due to the presence of about 1.1 and 1.3 per cent. of dinitroiodobenzene in the two cases; as the latter is formed only from *o*-iodonitrobenzene under the given conditions, it can be expressed as such, and the values just given for the proportions of *o*- and *p*-compounds are corrected on this basis. W. A. D.

**Velocity of Substitution of a Halogen by an Alkoxy Group in some Aromatic Halogen Nitro-compounds.** By P. K. LULOFFS (*Rec. Trav. Chim.*, 1901, 20, 292—327. Compare Steger, Abstr., 1899, i, 745).—The method of procedure adopted was the same as that of Steger (*loc. cit.*), the special points studied being the interaction of 1-chloro- and 1-bromo-2 : 4-dinitrobenzenes with sodium methoxide and ethoxide, and of 1-iodo-2 : 4-dinitrobenzene and several other nitro-compounds with sodium ethoxide. The influence of the concentration of the alcoholic solution, the addition of water to the alcohol, the presence of a salt of sodium, and the temperature on the velocity constant,  $k$ , of the equation  $-dc/dt = kc^2$ , was determined; the results are given in the form of tables and curves, and in the following résumé.

The transformation of the monohalogen dinitrobenzenes  $[\text{X} : (\text{NO}_2)_2 =$   
 $h \quad 2$

1 : 2 : 4] by an alkyl oxide takes place in only one direction, the halogen in position 1 being substituted quantitatively by the alkoxyl group; the velocity of replacement by ethoxyl is greater than that by methoxyl, and the substitution of chlorine easier than that of bromine, and much easier than that of iodine. Thus, for sodium ethoxide in an absolute alcoholic solution containing three-fifths of the gaseous concentration of the halogen dinitrobenzene at 15°, the values of  $k$  for chlorine, bromine, and iodine were 3.26, 2.04, and 0.455, and the times in which the reaction was one-half complete, 17.7, 35, and 128 minutes respectively. Iodine is thus much more firmly attached to the aromatic nucleus than bromine, and bromine than chlorine.

By comparison with Steger's results, it appears that the replacement of a nitro-group in *o*- or *p*-dinitrobenzene, occurs much more slowly than that of the chlorine atom in chloro-2 : 4-dinitrobenzene. Contrary to Steger's results, diminishing the concentration increases the velocity constant; this increase is greater in the case of the chloro- than in that of the bromo-compound, and for absolute ethyl than for absolute methyl alcohol. The effect of changing the concentration is thus the same as in the case of the reaction  $\text{MeI} + \text{NaOEt} = \text{MeOEt} + \text{NaI}$  (Hecht, Conrad, and Brückner, Abstr., 1890, 1046).

When the alcohols employed are diluted with water, there is a definite coefficient for each dilution, even when the quantity of water is as great as 40 per cent. The addition of water diminishes the reaction constant in the case of sodium ethoxide, and initially slightly increases that of sodium methoxide, but in the latter case subsequent diminution occurs. The influence of dilution is most marked with chlorodinitrobenzene and least with iododinitrobenzene (compare Lobry de Bruyn and Steger, Abstr., 1899, i, 745).

The addition of sodium bromide or acetate to alcoholic sodium ethoxide diminishes the velocity of interaction of the latter with 1-bromo-2 : 4-dinitrobenzene; the influence of the bromide is much the greater, and is especially notable in the cases where the alcohol is diluted with water. The temperature coefficient of the action of sodium ethoxide and 1-chloro-2 : 4-dinitrobenzene is 1.28, and for 1-bromo-2 : 4-dinitrobenzene, 1.41.

The speed of replacement of chlorine in *p*-nitrobenzyl chloride is greater than in *o*-nitrobenzyl chloride; the action of sodium ethoxide and *p*-nitrobenzonitrile does not give a definite velocity constant because both the nitro- and cyano-group undergo replacement. The action of the ethoxide on *p*- or *m*-nitrobenzoyl chloride at 0° is too rapid for measurement. W. A. D.

**Molecular Weight of Nitrosoaryls.** By EUGEN BAMBERGER and ADOLF RISING (*Ber.*, 1901, 34, 3877—3880).—Nitrosobenzene, *o*- and *p*-bromonitrosobenzene, *o*- and *p*-nitrosotoluene, nitroso-*p*-xylene, and 1-nitroso-2 : 4-xylene were found to give normal values for the mol. weight, both in freezing benzene and in boiling acetone; these substances all dissolve with a bluish-green or green colour. Nitrosomesitylene gave  $M = 180.4$  in boiling acetone and  $M = 233$  (mean value) in freezing benzene, the calculated value being  $M = 149$ ; similarly, 1-nitroso-2 : 6-xylene gave  $M = 188$  (mean value) in boiling acetone and  $M = 237$  (mean

value) in freezing benzene, the calculated value being  $M = 135$ . The indications of polymerisation to a double molecule which are thus afforded correspond closely with observations made on the colour of the solutions; both substances dissolve in the cold with an exceedingly faint bluish-green colour, which becomes darker on heating, as the colourless polymeride dissociates, and gradually becomes less intense when cooled, the polymerisation taking place only slowly. It is noteworthy that only the diortho-derivatives of nitrosobenzene are polymerised; for similar observations in the fatty series, compare Piloty (Abstr., 1898, i, 289).

The only derivative of nitrosobenzene which appears to be unimolecular in the solid state is 3:4-dimethylnitrosobenzene (Abstr., 1901, i, 529), which forms a clear, bluish-green solid. T. M. L.

**Diphenyl Derivatives.** By FRITZ ULLMANN and W. RUSSEL FORGAN (*Ber.*, 1901, **34**, 3802—3805. Compare Abstr., 1901, i, 586).—On adding a solution of *o*-nitrobenzenediazonium chloride to a cold solution of cuprous chloride, a small quantity (17 per cent.) of *o*-chloronitrobenzene is formed, together with a much larger quantity (68 per cent.) of 2:2'-dinitrodiphenyl. By this method, 4:4'-dichloro-2:2'-dinitrodiphenyl was obtained from 4-chloro-2-nitroaniline (yield 59 per cent.) and 2:2'-dinitro-4:4'-ditolyl from 3-nitro-*p*-toluidine (yield 88 per cent.).

5:5'-Dichloro-2:2'-dinitrodiphenyl,  $C_{12}H_6Cl_2(NO_2)_2$ , prepared from 3-chloro-6-nitroaniline, crystallises in pale yellowish-brown needles melting at  $170^\circ$ . K. J. P. O.

**Basic Properties of Carbon and the Constitution of the so-called Triphenylmethyl.** By FRIEDRICH KEHRMANN and F. WENTZEL (*Ber.*, 1901, **34**, 3815—3819. Compare Gomberg, Abstr., 1901, i, 77, 319, 638; Norris and Sanders, *ibid.*, i, 198).—Triphenylchloromethane dissolves in cold concentrated sulphuric acid, evolving hydrogen chloride and yielding a golden-yellow solution; when diluted with water, the solution remains yellow, but on further dilution becomes colourless and gives a colourless precipitate of triphenylcarbinol. Similarly, when concentrated hydrochloric acid is added to a colourless ethereal solution of triphenylcarbinol, the solution first becomes yellow and finally colourless, yielding ordinary triphenylchloromethane. The authors conclude that triphenylchloromethane and similar compounds exist in two forms, namely,  $CPh_3Cl$ , colourless, and  $CHCl \begin{smallmatrix} <CH:CH> \\ <CH:CH> \end{smallmatrix} C:CPh_2$ , yellow. It is from the latter that Gomberg's triphenylmethyl or rather diphenylphenylenemethane is obtained by the loss of  $HCl$ . The bivalent carbon atom would thus possess basic properties.

*p*-Rosaniline chloride and dichromate are both anhydrous, and are obtained from the carbinol by the loss of water. The chloride reacts with concentrated sulphuric acid, yielding a golden-yellow solution, which, on diluting with ice and water, becomes paler and finally colourless. When boiled, it turns purple, but becomes colourless again on cooling.

A yellow compound,  $CPh_3Cl, SnCl_4$ , is described.

J. J. S.

**Some Relation between Physical Constants and Constitution in Benzenoid Amines.** By WILLIAM R. HODGKINSON and LEONARD LIMPACH (*Chem. News*, 1901, 84, 221—222).—The investigations on the relationship between melting points and constitution in some amines (*Proc.*, 1893, 41; *Trans.*, 1901, 79, 1080) have been continued and it is observed that the differences between the melting points of the formyl and acetyl derivatives of bases of the same constitution is constant or nearly so, moreover that this relationship is not disturbed by the replacement of a methyl group by an ethyl or methoxy-group, although, of course, the melting points of the latter compounds differ from those of the methyl compounds. Furthermore, the melting points of the formyl and acetyl derivatives of the tetramethyl bases correspond with the sum of the melting points of two xyldines less the melting point of formanilide. D. A. L.

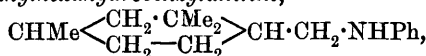
**Preparation of Hexahydrobenzylamines.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 121976).—*Homocamphanylaniline*,  $\text{CH}_2 \cdot \text{CH} \text{---} \text{CH} \cdot \text{CH}_2 \cdot \text{NHPh}$

$\begin{array}{c} | \quad \text{CMe}_2 \quad | \\ \text{CH}_2 \cdot \text{CMe} \text{---} \text{CH}_2 \end{array}$ , obtained from the corresponding un-

saturated amine *homocamphenylaniline*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH} \text{---} \text{CH} \cdot \text{CH}_2 \cdot \text{NHPh} \\ | \quad \text{CMe}_2 \quad || \\ \text{CH}_2 \cdot \text{CMe} \text{---} \text{CH} \end{array}$ ,

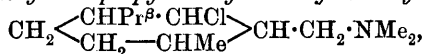
or its additive product with hydrogen chloride by reduction with sodium and ethyl alcohol, is a viscid, colourless oil boiling at 220° under 20 mm. pressure.

2 : 2 : 4-*Trimethylhexahydrobenzylamine*,



prepared by reducing 2 : 2 : 4-trimethyltetrahydrobenzylamine or its additive compound with hydrogen chloride, boils at 190° under 15 mm. pressure.

6-*Chloro-2-methyl-5-isopropylhexahydrobenzylidimethylamine*,



produced by the action of phosphorus oxychloride on 6-hydroxy-2-methyl-5-isopropylhexahydrobenzylidimethylamine (b. p. 140° under 14 mm. pressure), is a colourless oil, and on reduction with zinc dust and acetic acid containing a little hydrochloric acid it yields 2-methyl-5-isopropylhexahydrobenzylidimethylamine, this base being a colourless oil having an odour resembling that of coniine and boiling at 118—120° under 15—16 mm. pressure.

2-Methyl-5-isopropylhexahydrobenzylamine, 2-methyl-5-isopropylhexahydrobenzylamine, and 2-methyl-5-isopropylhexahydrobenzylethylamine, obtained by reducing the corresponding unsaturated bases or their hydrogen chloride derivatives, are colourless oils boiling respectively at 215° (under 33 mm. pressure), and 226—228° and 135—140° under the ordinary pressure.

p-Methylhexahydrobenzylamine is a colourless oil boiling at 195° under 30 mm. pressure. G. T. M.

**New Bases from Anhydroformaldehydeaniline [Methyleneaniline] and its Homologues.** ERNST ERDMANN (D.R.-P. 121506).—Isomerides of the anhydroformaldehyde bases are produced by dissolving these substances in glacial acetic acid at temperatures below  $25^{\circ}$ , and are isolated as amorphous precipitates on diluting the products with water. The compound,  $(C_7H_7N)_x$ , from methyleneaniline, is a pale yellow powder having no definite melting point; it yields an *acetyl* derivative,  $(C_7H_6NAc)_x$ , and when reduced with zinc dust yields a mixture of aniline and *p*-toluidine in approximately equal proportion. The corresponding *o*-toluidine and *p*-xylylene compounds form white powders melting at  $150^{\circ}$  and  $85$ — $90^{\circ}$  respectively. The *p*-toluidine and *m*-xylylene derivatives are tarry substances. These compounds dissolve in dilute hydrochloric acid, and with the substantive cotton colouring matters form lakes which are comparatively stable to acids.

G. T. M.

**Preparation of Aromatic Bases [by the aid of Formaldehyde].** ERNST ERDMANN (D.R.-P. 122474. Compare Troeger, Abstr., 1888, 286).—When 4-*m*-xylylene, *p*-toluidine, or *p*-chloroaniline is treated with formaldehyde solution in the presence of moderately strong hydrochloric acid, a substance is obtained possessing the property of forming lakes with the substantive cotton colouring matters, and thereby rendering these less sensitive to dilute acids. The *m*-xylylene and *p*-toluidine derivatives are yellow, amorphous substances melting respectively at  $62$ — $65^{\circ}$  and at  $65$ — $70^{\circ}$ . In the latter case, the crystalline base described by Troeger is obtained as a by-product. *p*-Chloroaniline gives rise to a yellow, crystalline derivative melting at  $188^{\circ}$ , the hydrochloride of which separates from water in colourless prisms.

G. T. M.

**Mono- and Di-alkylated Aromatic Amines.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 121683. Compare Abstr., 1901, i, 695 699).—Methylnaphthionic acid (1-methylaminonaphthalene-4-sulphonic acid),  $NHMe \cdot C_{10}H_6 \cdot SO_3H$ , obtained by heating sodium  $\alpha$ -naphthol-4-sulphonate with a 10 per cent. solution of methylamine sulphite,  $SO_3(NH_3Me)_2$ , at  $150^{\circ}$  and acidifying the product, separates from solution in a crystalline form. This operation may be performed in two stages; the first consists in converting the naphtholsulphonate into its sulphurous ester by means of sodium hydrogen sulphite, and the second in treating this product with methylamine.

Sodium  $\beta$ -naphthol-6-sulphonate, when heated for 15 hours at  $125^{\circ}$  with an aqueous solution of methylamine and methylamine sulphite, readily yields sodium 2-methylaminonaphthalene-6-sulphonate, from which dilute acids liberate the crystalline sulphonic acid. Dimethyl-*m*-aminophenol is readily produced by treating resorcinol with a solution of dimethylamine and its sulphite at  $125^{\circ}$  and is isolated from the product in the form of its hydrochloride.

G. T. M.

**Preparation of  $\beta$ -Naphthylamine Derivatives.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 122570. Compare Abstr., 1901, i, 695, 699).—*Phenyl- $\beta$ -naphthylamine-6-sulphonic acid*, produced by

heating together sodium  $\beta$ -naphthol-6-sulphonate, aniline, and sodium hydrogen sulphite solution, is readily soluble in water and yields a bluish-violet azo-compound with diazotised *p*-nitroaniline.

2:5-Dihydroxynaphthalene-7-sulphonic acid, when treated in this manner, yields an amino-acid which is probably 2-phenylamino-5-hydroxynaphthalene-7-sulphonic acid. 2-*o*-Tolylamino-8-hydroxynaphthalene-6-sulphonic acid is obtained from 8-hydroxy- $\beta$ -naphthylamine-6-sulphonic acid, *o*-toluidine, and sodium hydrogen sulphite. 2-*o*-Xylamino-5-hydroxynaphthalene-7-sulphonic acid is produced from *o*-xylydine and 5-hydroxy- $\beta$ -naphthylamine-7-sulphonic acid. Similar substituted  $\beta$ -naphthylamine derivatives are obtained from  $\beta$ -naphthol-6-sulphonic acid and *p*-phenylenediamine, and also from 8-hydroxy- $\beta$ -naphthylamine-6-sulphonic acid and *p*-aminophenol. G. T. M.

**Naphthalenoid Thiocarbamides containing Hydroxyl Groups.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 122286. Compare D.R.-P. 116201 and 116200).—Thiocarbonyldihydroxydinaphthylamine-disulphonic acids,  $\text{CS}[\text{NH}\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{SO}_3\text{H}]_2$ , are obtained by the action of carbon disulphide, sulphur, and sodium carbonate solution on the aminonaphthols and their sulphonic acids in which the amino- and hydroxy-radicals are present in positions other than 1:2 or 1:8 with respect to each other. G. T. M.

**Preparation of Tertiary Aromatic Bases from their Alkyl Haloids.** By JOHANNES PINNOW (*Ber.*, 1901, 34, 3772).—A claim for priority in the use of the method for converting aromatic quaternary salts into the corresponding tertiary bases by heating with aqueous ammonia (compare Abstr., 1898, i, 184; 1899, i, 588, and Scholtz, Abstr., 1898, i, 567; 1901, i, 749). G. T. M.

**Derivatives of Phenyl Ether. II.** By ALFRED N. COOK (*J. Amer. Chem. Soc.*, 1901, 23, 806—813. Compare Abstr., 1901, i, 144).—*o*-Nitrophenyl *o*-tolyl ether,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\text{Me}$ , obtained by the action of *o*-bromonitrobenzene on potassium *o*-tolyl oxide, is a dark red liquid which boils at 194—196° under 14 mm. and decomposes when heated under atmospheric pressure; it is not volatile with steam, has an oily taste, a sp. gr. 1.195 at 20°, and is soluble in the usual organic solvents. On reduction with tin and hydrochloric acid, the hydrochloride of *o*-aminophenyl *o*-tolyl ether is produced as a white, waxy mass; the base could not be isolated on account of its instability. By the action of sulphuric acid on *o*-nitrophenyl *o*-tolyl ether, a sulphonic acid,  $\text{NO}_2\cdot\text{C}_{12}\text{H}_7\cdot\text{OMe}\cdot\text{SO}_3\text{H}$ , is produced, which is a reddish-yellow, viscous liquid, soluble in 2.5 parts of water at 80°, and readily so in alcohol, benzene, or light petroleum; the barium, strontium, and lead salts are soluble in water to the extent of 0.745, 2, and 8.17 per cent. at 100°, and 0.12, 0.68, and 3.5 per cent. at 31° respectively.

*o*-Nitrophenyl *m*-tolyl ether is a red, oily liquid which boils at 223° under 30 mm., but decomposes if heated under atmospheric pressure; it is not volatile with steam, has a sp. gr. 1.208 at 27°, and is readily soluble in the usual organic solvents. *o*-Aminophenyl *m*-tolyl ether hydrochloride is a clear, viscous substance, readily soluble in alcohol or

ether and sparingly so in water; the base is very unstable and could not be isolated. *o*-Nitrophenyl-*m*-tolyl-ether-sulphonic acid crystallises in short, yellowish-brown needles, and is soluble in water, alcohol or ether; the barium salt is soluble in water to the extent of 1.1 per cent. at 82° and 0.61 per cent. at 35°.

*o*-Nitrophenyl-*p*-tolyl-ether-sulphonic acid forms reddish-brown crystals, soluble to the extent of 9.8 per cent. in water at 31°, and readily soluble in alcohol, ether, benzene, or glacial acetic acid; the barium salt is soluble in water to the extent of 69.1 per cent. at 80° and 14.7 per cent. at 27°. E. G.

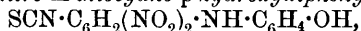
**Ethoxyisoeugenol** (Monoethoxymethylpropenylcatechol Ether). CÆSAR POMERANZ (D.R.-P. 122701. Compare Abstr., 1892, 972).—*Ethoxyisoeugenol* (2-monoethoxymethyl-4-propenylcatechol ether),  $\text{OEt} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CH} : \text{CHMe}$ , results from the action of alcoholic potassium hydroxide solution on saffrole at 140–150°; it is a colourless, almost odourless oil boiling at 172° under 22 mm. pressure.

G. T. M.

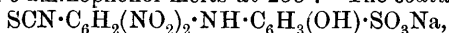
**isoChavibetol**. CÆSAR POMERANZ (D.R.-P. 123051. Compare Abstr., 1901, i, 699).—The condensation products of the alcohols with isosaffrole having the general formula  $\text{OR} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CH} : \text{CHMe}$  yield isochavibetol when treated with dilute alcoholic solutions of the mineral acids.

G. T. M.

**Substituted Thiocyanates of the *o*-*p*-Dinitrohydroxydiphenylamines**. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 122569).—1 : 3-Dithiocyano-4 : 6-dinitrobenzene, obtained by adding powdered potassium thiocyanate or the corresponding salt of another metal to an acetone solution of 1 : 3-dichloro-4 : 6-dinitrobenzene, crystallises from alcohol in pale yellow leaflets and decomposes at 185°. When this compound is treated with a mixture of sodium acetate, alcohol, and an aminophenol for 8 hours at 65°, one of the thiocyano-groups is removed and a diphenylamine derivative is produced. *o*-*p*-Dinitro-*m*-thiocyano-*p*-hydroxydiphenylamine,



obtained from *p*-aminophenol, separates from acetone, alcohol, or glacial acetic acid in red crystals melting at 227–228°; the corresponding compound from *o*-aminophenol melts at 255°. The sodium salt,



of the *p*-aminophenol-*o*-sulphonic acid derivative crystallises in reddish-brown needles; the aminosalicylic acid compound is a yellowish-brown powder; these substances decompose without melting. G. T. M.

**Preparation of Chlorides and Anhydrides of the Carboxy-acids**. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 123052).—When 1 mol. of an aromatic sulphonic chloride is heated with 1 mol. of the anhydrous salt of a carboxylic acid, the corresponding acid chloride is formed in accordance with the following equation:  $\text{Ph} \cdot \text{SO}_2\text{Cl} + \text{R} \cdot \text{CO}_2\text{Na} = \text{Ph} \cdot \text{SO}_3\text{Na} + \text{R} \cdot \text{COCl}$ . If 2 mols. of the anhydrous salt are employed, the corresponding anhydride is produced. Acetyl chloride and acetic

anhydride are obtained by the action of *p*-toluenesulphonic chloride on 1 and 2 mols. of sodium acetate respectively. Propionic and benzoic anhydrides and salicylyl chloride may also be prepared by this process.

G. T. M.

**Phenylglycine-*o*-carboxylic Acid.** DANIEL VORLÄNDER and RUDOLF VON SCHILLING (D.R.-P. 121287).—Nitroso-*o*-tolylglycine,  $C_6H_4Me \cdot N(NO) \cdot CH_2 \cdot CO_2H$ , an oil obtained by treating *o*-tolylglycine with sodium nitrite and dilute sulphuric acid, yields nitrosophenylglycine-*o*-carboxylic acid (m. p.  $120^\circ$ ) on treatment with potassium permanganate solution; the oxidation product when reduced with zinc dust and sodium hydroxide or sulphurous acid, or when boiled with alcoholic hydrogen chloride, gives rise to phenylglycine-*o*-carboxylic acid (compare Abstr., 1900, i, 295, and 1901, i, 462, 463).

G. T. M.

**Electric Conductivity of Chloro- and Bromo-nitrobenzoic Acids.** By ARNOLD F. HOLLEMAN and B. R. DE BRUYN (*Rec. Trav. Chim.*, 1901, [ii], 20, 360—364).—The following table gives a comparison of the affinity constants, *k*, of chloro- and bromo-nitrobenzoic acids as determined with carefully purified material and as calculated by Ostwald and Bethmann's method:

Acid.	Structure. $CO_2H : X : NO_2$ .	<i>k</i> calc.	Found $\mu_\infty$ .	<i>k</i> found.
Chloronitrobenzoic .....	1 : 2 : 5	0.75	356	0.62
„ .....	1 : <del>2</del> : 3	0.75	356	0.87
„ .....	1 : 3 : 6	1.60	356	1.42
„ .....	1 : 3 : 2	1.60	356	0.44
Bromonitrobenzoic .....	1 : 2 : 5	0.83	353	0.91
„ .....	1 : 2 : 3	0.83	353	1.16
„ .....	1 : 3 : 6	1.41	355	1.55
„ .....	1 : 3 : 2	1.41	353	0.34

There is a satisfactory agreement between observed and calculated values except in the case of the 1 : 3 : 2-acids. In the original paper, a table is given showing a similar comparison of a large number of other disubstituted benzoic acids, and here again satisfactory agreement is visible except in the case of  $\alpha$ -nitrophthalic acid (calc. 12.4, found 1.22),  $\beta$ -resorcylic acid (calc. 1.73, found 5.0) and *o*-nitrosalicylic acid (calc. 0.58, found 1.57). In all cases where a divergence occurs, the position of the groups is adjacent. It is true that *o*-chloro- and *o*-bromo-*m*-nitrobenzoic acids and hydroxysalicylic acid [ $CO_2H : (OH)_2 = 1 : 2 : 3$ ] give a good agreement, but here the halogen or hydroxyl is in the ortho-position relatively to the carboxyl; when a great divergence occurs it is the nitro-group which is in this position.

W. A. D.

**Anthranil.** By OTTO BUHLMANN and ALFRED EINHORN (*Ber.*, 1901, 34, 3788—3793).—The substance obtained by Einhorn and Bull



(Abstr., 1897, i, 345) by the action of hydroxylamine hydrochloride on anthranil in alcoholic solution is shown to be the oxime of *o*-aminobenzaldehyde, and not the oxime of anthranil; the hydroxylamine has acted as a reducing agent.

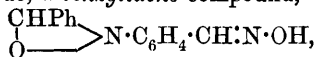
Free hydroxylamine and anthranil yield a *compound*,  $C_7H_8O_2N_2$ , which crystallises from benzene in white, prismatic needles melting at  $114-115^\circ$ , and is not the oxime of anthranil, but probably *o*-hydroxyaminobenzaldehyde; it dissolves in dilute alkalis and acids, and is quantitatively converted by the latter into anthranil. With benzaldehyde, it gives a condensation *product*,  $C_{14}H_{12}O_2N_2$ , which crystallises in pale yellow, prismatic needles melting and decomposing at  $164^\circ$ .

Hydrazine hydrate and anthranil react in the presence of alcohol at  $100^\circ$  to form a *compound*,  $C_7H_9ON_3$ , which crystallises in pale-yellow, transparent, prismatic leaflets melting and decomposing at  $120^\circ$ ; dilute acids immediately decompose it into anthranil and a hydrazine salt.

From phenylhydrazine and anthranil a *compound*,  $C_{13}H_{13}ON_3$ , is obtained as yellow, prismatic needles, which darken at  $140^\circ$ , and melt and decompose at  $155^\circ$ ; when boiled with acetic acid, or heated alone, it is converted into the phenylhydrazone of *o*-aminobenzaldehyde.

Other compounds, besides anthranil, which contain the group  $\cdot CO \cdot NH \cdot$ , are able to combine with hydrazines without elimination of water; thus when benzamide and phenylhydrazine are heated at  $100^\circ$  in acetic acid solution, *acetylbenzamidophenylhydrazone hydrate*,  $NHPh \cdot NH \cdot CPh(NH_2) \cdot O \cdot COMe$ , is formed, and crystallises from benzene in white, silky needles melting at  $105^\circ$ ; acids decompose it into phenylhydrazine, acetic acid, and benzamide. K. J. P. O.

**Constitution of Anthranil.** By EUGEN BAMBERGER and ED. DEMUTH (*Ber.*, 1901, 34, 4015—4028. Compare Buhlmann and Einhorn, preceding abstract).—When anthranil (1 mol.) and hydroxylamine, (3 mols). are heated together in solution in absolute alcohol, *o*-hydroxyaminobenzaldoxime,  $OH \cdot NH \cdot C_6H_4 \cdot CH : N \cdot OH$ , is formed; this substance can also be obtained by reduction of *o*-nitrobenzaldoxime with zinc dust; it crystallises in long, white, silky needles melting at  $120-121^\circ$ , is soluble in alkalis with a lemon-yellow colour, and reduces silver nitrate and Fehling's solution. In dilute acids, it dissolves, and is then converted into anthranil and hydroxylamine. With aldehydes, it condenses; thus with benzaldehyde, a *benzylidene* compound,



is formed which crystallises in lustrous needles melting at  $172-172.5^\circ$ ; the *p*-nitrobenzylidene compound crystallises in small, silky needles; both substances dissolve in alkali hydroxides with an intense red coloration.

Molecular proportions of anthranil and hydroxylamine, dissolved in dilute alcohol, gave mainly *o*-azoxybenzaldoxime,  $ON_2(C_6H_4 \cdot CH : NOH)_2$ , which crystallises in needles melting at  $210.5-211^\circ$ ; this azoxy-compound was also prepared from *o*-azoxybenzaldehyde and hydroxylamine.

When 2 mols. of hydroxylamine interact with 1 mol. of anthranil, besides *o*-azoxybenzaldoxime, *o*-triazobenzaldoxime, *o*-aminobenzaldoxime, and benzaldoxime are formed. Prolonged action of a still greater

excess of hydroxylamine on anthranil produces mainly *o*-aminobenzaldoxime together with the other substances just mentioned.

In the presence of potassium hydroxide, hydroxylamine and anthranil yield *o*-nitro- and *o*-amino-benzaldoxime.

The view is expressed that the first action of hydroxylamine on anthranil is one of hydration,  $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{N} \\ \text{CH}\end{smallmatrix}\right\rangle\text{O} + \text{H}_2\text{O} = \text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{NH}\cdot\text{OH} \\ \text{CHO}\end{smallmatrix}\right\rangle$ . From the hydroxylaminobenzaldehyde, *o*-aminobenzaldehyde, *o*-nitrobenzaldehyde, and *o*-azoxybenzaldehyde would be produced respectively by oxidation or reduction. It is suggested that the *o*-triazobenzaldehyde is produced by union of the group  $\text{CHO}\cdot\text{C}_6\text{H}_4\cdot\text{N}:$  (formed from anthranil) and molecular nitrogen, which arises by oxidation of the hydroxylamine (compare this vol., i, 25). In the presence of excess of hydroxylamine, these aldehydes would be converted into oximes.

K. J. P. O.

**Methyl Methylanthranilate.** SCHIMMEL & Co. (D.R.-P. 122568).—*Methyl methylanthranilate*,  $\text{NHMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ , prepared either by treating methylanthranilic acid with methyl alcohol and concentrated hydrochloric or sulphuric acid, or by heating sodium or potassium anthranilate with potassium hydroxide and methyl iodide under pressure, boils at 130—131° under 13 mm. pressure, and has a sp. gr. 1.120 at 15°; its solution has a blue fluorescence. This ester has the characteristic odour of mandarin oil, and is contained in this essence to the extent of 1.5 per cent.

G. T. M.

**Preparation of *o*-Benzoicsulphimide ("Saccharin") and other Aromatic Sulphonamides.** BASLER CHEMISCHE FABRIK (D.R.-P. 122567).—Benzene- and *o*-toluene-sulphinic acids, dissolved in a mixture of alcohol and excess of aqueous ammonia and treated with chlorine at 35—40°, yield the corresponding amides. *o*-Benzoicsulphimide ("saccharin") is obtained by this process in one operation, and from monomethyl *o*-carboxybenzenesulphinate,  $\text{SO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$  (m. p. 98—99°), the latter substance being produced from diazotised methyl anthranilate by the action of alcoholic sulphurous acid and copper sulphate.

G. T. M.

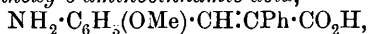
**Stable Carbonyl Derivatives of Indigo-white.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 121866).—The normal carbonic ester of indigo-white is produced on treating a mixture of indigo-white, acetone, and sodium hydroxide solution with carbonyl chloride; it decomposes without melting, yielding indigotin, and is hydrolysed by warming with dilute solutions of the alkali hydroxides. The product of the action of methyl or ethyl chlorocarbonate on indigo-white in the presence of alkali hydroxides, when extracted with alcohol, yields an insoluble *ester* crystallising from acetone in felted needles and melting at 257—259°; the alcoholic extract contains a second *ester* separating in needles and melting at 110—112°. These esters are also obtained along with the infusible product by treating indigo-white with carbonyl chloride in aqueous sodium hydroxide solution.

G. T. M.

**Phenanthrene Derivatives.** By ROBERT PSCHORR (*Ber.*, 1901, 34, 3998—4007).—[With C. SEYDEL.]—The hitherto unknown

2-methoxyphenanthrene was synthesised by condensing 6-nitro-3-methoxybenzaldehyde with sodium phenylacetate in the presence of acetic anhydride at 100°; the *α*-phenyl-β-6-nitro-3-methoxycinnamic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{CH} : \text{CPh} \cdot \text{CO}_2\text{H}$ , thus obtained crystallises in pale yellow leaflets melting at 165—166°, and yields sparingly soluble silver, lead, and calcium salts, which all crystallise in needles.

*α*-Phenyl-β-3-methoxy-6-aminocinnamic acid,



obtained by reducing the corresponding nitro-compound with ferrous sulphate in presence of ammonia, crystallises in greyish-violet leaflets having a silvery lustre, which become coloured at 182—187° and melt at 227—228°; this substance forms well-crystallised salts both with acids and bases.

*α*-Phenyl-β-6-diazo-3-methoxycinnamic acid was obtained in the form of the sulphate from the last-mentioned substance; the sulphate crystallises in yellow prisms which explode at 140—150°. On boiling the aqueous solution of the sulphate and gradually adding sodium carbonate, 2-methoxyphenanthrene-9-carboxylic acid is obtained; it crystallises in lustrous prisms or needles melting at 228°, and exhibits in solution a blue fluorescence; the ammonium, silver, ferric, cupric, and lead salts are crystalline and sparingly soluble. 2-Methoxyphenanthrene is prepared from the acid by distilling it under 100 mm. pressure; it crystallises in lustrous leaflets melting at 99°, and, in solution, exhibits a faint blue fluorescence; the *picrate* crystallises in orange needles melting at 124°.

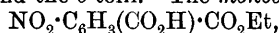
[With AUGUST KLEIN.]—From the sulphonic acids obtained from phenanthrene, two were isolated by fractional crystallisation of the lead salts, which crystallise respectively with 2 and 3  $\text{H}_2\text{O}$ . From the sulphonic acid, which corresponds with the lead salt, crystallising with 2  $\text{H}_2\text{O}$ , a *phenanthrol* was prepared by fusion with 50 per cent. potassium hydroxide; it crystallises in lustrous leaflets melting at 168°; its *acetyl* derivative crystallises in needles melting at 141°; its methyl ether is identical with the 2-methoxyphenanthrene just described. The hydroxyl group is therefore in position 2. This phenanthrol is identical with the compound obtained by Werner and Kunz (Abstr., 1901, i, 696) from phenanthrylamine, the constitution of which is therefore confirmed.

2-Methoxyphenanthrene, unlike the 3- and 4-derivatives, yields only a *monobromo*-derivative, which crystallises in needles melting at 176°. On oxidising 2-acetoxyphenanthrene with chromic acid, a *quinone*,  $\text{C}_{16}\text{H}_{10}\text{O}_4$ , is formed as yellowish-red crystals melting at 222°.

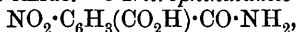
The lead phenanthrenesulphonate crystallising with 3  $\text{H}_2\text{O}$  yields 3-phenanthrol (Abstr., 1900, i, 487), which was recognised by preparation of the acetyl derivative and methyl ether (Abstr., 1900, i, 233). The latter gives a *dibromo*-derivative which crystallises in pale red needles melting at 150°. 3-Acetoxyphenanthrene, on oxidation, yields a *quinone*,  $\text{C}_{16}\text{H}_{10}\text{O}_4$ , which forms yellow leaflets melting at 206°; from the latter, on hydrolysis, is obtained 3-phenanthrolquinone,  $\text{C}_{14}\text{H}_8\text{O}_3$ , crystallising in yellowish-red needles which begin to decompose at 315° and finally melt at 330°. The temperatures quoted are corrected.

K. J. P. O.

**The Mononitrophthalic Acids.** By MARSTON T. BOGERT and LEOPOLD BOROSCHEK (*J. Amer. Chem. Soc.*, 1901, **23**, 740—761).—3-Nitrophthalic acid, when heated in a closed tube, melts at 222°, but in an open tube it decomposes at about 207° with formation of the anhydride. The aniline salt (Graebe and Buenzod, *Abstr.*, 1899, i, 762) crystallises in colourless needles and melts at 185—187°. The acid *o*-toluidine salt,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{H})_2 \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_4\text{Me}$ , forms slender, white needles, melts at 181°, and at a slightly higher temperature decomposes into water and the *o*-tolil. The *monoethyl* ester,



is a white, crystalline substance melting at 157°. The anhydride, obtained by heating the acid at 235—240° for 6—8 hours, crystallises in colourless needles and melts at 163°. The *imide*, prepared by the action of heat on the ammonium hydrogen salt, crystallises in pale yellow, lustrous needles, melts at 215—216°, and furnishes a white, crystalline *potassium* salt. The *amide* melts and decomposes at 200—201° with formation of the imide. 3-Nitrophthalamic acid,



obtained by heating the imide with baryta water at 80°, melts at 156° with production of the imide. The *ethylimide* crystallises in long, yellow needles and melts at 105°. The anil melts at 137°. The *anilic acid*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{H}) \cdot \text{CO} \cdot \text{NHPh}$ , forms pale yellow needles and melts at 180° with formation of the anil. The *o*-, *m*- and *p*-nitroanils melt at 167°, 219°, and 249° and the *o*-, *m*- and *p*-tolils at 145°, 129°, and 154° respectively. The *hydrazide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{smallmatrix}$  or

$\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{N} \cdot \text{NH}_2$ , forms pale yellow, microscopic crystals and melts and decomposes at about 320°. When 3-nitrophthalic anhydride is heated with phosphorus pentachloride, 3-chlorophthalic anhydride is produced, which on boiling with dilute hydrochloric acid yields the corresponding acid melting at 186°. 3-Chlorophthalimide crystallises in white needles; when heated in an open tube, it sublimes, but in a closed tube it melts at 118—120°.

4-Nitrophthalic acid is best prepared by the oxidation of *p*-nitrophthalide with alkaline potassium permanganate. When an alcoholic solution of 4-nitrophthalic anhydride is boiled for 8 hours, an *ethyl* ester,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{H}) \cdot \text{CO}_2\text{Et}$ , is produced which melts at 141—150°, and appears to be an isomeride of the ester (m. p. 127—128°) obtained by Miller (*Abstr.*, 1882, 404) by the action of hydrogen chloride on an alcoholic solution of the acid. The *imide* crystallises in pale yellowish-brown flakes, melts at 197°, and yields a *potassium* salt. The *amide* melts at 200° with formation of the imide. The *ethylimide* forms pale yellow scales and melts at 111—112°. The anil melts at 194°. The *anilic acid* forms pale yellow crystals, and melts at 181° with production of the anil. The *o*-, *m*- and *p*-nitroanils melt at 233°, 243°, and 251—253°, and the *o*-, *m*- and *p*-tolils at 160°, 197°, and 165° respectively. The *p*-tolilic acid crystallises in white needles, and melts at 172° with formation of the *p*-tolil. The *hydrazide* forms small yellow crystals, gives a white sublimate at 270°, darkens at 280°, and remains unmelted at 300°. 4:4'-Azophthalic acid, obtained by reduc-

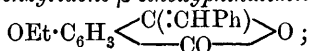
ing 4-nitrophthalic acid with sodium amalgam, forms a salmon-coloured, crystalline powder, does not melt at  $360^{\circ}$ , and furnishes a red, crystalline *silver* salt which is insoluble in hot water; if, however, the azophthalic acid is prepared by the oxidation of 5:5'-azophthalide with potassium permanganate, it melts and decomposes at  $285\text{--}300^{\circ}$ , and yields a silver salt soluble in hot water. 5:5'-Azophthalide, obtained by the reduction of *p*-nitrophthalide with sodium amalgam, forms small, red crystals and melts and decomposes at  $260\text{--}280^{\circ}$ . E. G.

**Derivatives of the Two Nitrophthalic Acids.** By PAUL ONNERTZ (*Ber.*, 1901, 34, 3735—3747).— $\beta$ -Ethoxyphthalylacetic acid,

$\text{OEt}\cdot\text{C}_6\text{H}_3\begin{matrix} \diagup \\ \text{CO} \end{matrix}\text{C}:\text{CH}\cdot\text{CO}_2\text{H}$ , prepared by heating ethoxyphthalic anhydride with acetic anhydride and sodium acetate, forms small, yellow needles, melts at  $246\text{--}248^{\circ}$  and does not dissolve in water. Benzyl-

idene- $\beta$ -ethoxyphthalide,  $\text{OEt}\cdot\text{C}_6\text{H}_3\begin{matrix} \diagup \\ \text{CO} \end{matrix}\text{C}(\text{CHPh})\text{O}$ , prepared from ethoxyphthalic anhydride and phenylacetic acid, forms prismatic crystals and melts at  $133\text{--}134^{\circ}$ . When warmed with potassium hydroxide, it is converted into 4-(or 5-)ethoxydeoxybenzoin-2-carboxylic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OEt})\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$ , which crystallises from a large bulk of hot water in minute, white prisms and melts at  $95\text{--}96^{\circ}$ ; with alcoholic potassium hydroxide or sodium ethoxide, on the other hand,

6-ethoxy-2-phenyl-1:3-diketohydrindene,  $\text{OEt}\cdot\text{C}_6\text{H}_3\begin{matrix} \diagup \\ \text{CO} \end{matrix}\text{CHPh}$ , is obtained, which crystallises from boiling alcohol in yellow plates and melts at  $172^{\circ}$ ; with alcoholic ammonia, 4-(or 5-)ethoxydeoxybenzoin-2-carboxylamide is formed, which crystallises from aqueous alcohol in well-formed, rhombic prisms, melts at  $149\text{--}151^{\circ}$ , and is converted by acetyl chloride into benzylidene- $\beta$ -ethoxyphthalimidine,

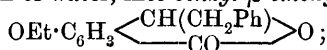


this separates from dilute acetic acid in yellow flakes and melts at  $160\text{--}162^{\circ}$ .

With hydroxylamine, ethoxydeoxybenzoincarboxylic acid gives the oximino-lactone of benzyl-4-(or 5-)ethoxyphenylketoxime-2-carboxylic acid,

$\text{OEt}\cdot\text{C}_6\text{H}_3\begin{matrix} \diagup \\ \text{CO} \end{matrix}\text{C}(\text{CH}_2\text{Ph})\text{N}=\text{O}$ , which crystallises from alcohol in long, transparent, prismatic tablets and melts at  $112^{\circ}$ . With phenylhydrazine, it gives 6-(or 7-)ethoxy-1-benzyl-3-phenylphthalazone,

$\text{OEt}\cdot\text{C}_6\text{H}_3\begin{matrix} \diagup \\ \text{CO} \end{matrix}\text{C}(\text{CH}_2\text{Ph})\text{NPh}=\text{N}$ , which crystallises from hot alcohol in pale yellow needles and melts at  $126\text{--}127^{\circ}$ . With sodium amalgam, the first product is  $\alpha$ -hydroxy-4-(or 5-)ethoxydibenzyl-2-carboxylic acid,  $\text{OEt}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Ph}$ , which readily, passes by loss of a molecular proportion of water, into benzyl- $\beta$ -ethoxyphthalide,



this crystallises from alcohol in microscopic prisms and melts at  $87\text{--}88^{\circ}$ . 4-(or 5-)Ethoxystilbene-2-carboxylic acid,  $\text{OEt}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{K})\cdot\text{CH}:\text{CHPh}$ , isomeric with the preceding compound, is formed when the hydroxy-

acid is heated with potassium hydroxide at  $213^{\circ}$ ; it crystallises from alcohol in small needles and melts at  $172^{\circ}$ . 4- (or 5-) *Ethoxydibenzyl-2-carboxylic acid*,  $\text{OEt}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$ , prepared by reducing ethoxystilbenecarboxylic acid with sodium amalgam, separates from alcohol in long, silky needles and melts at  $117^{\circ}$ . 4-Bromo-6-(or 7-)

*ethoxy-3-phenyldihydroisocoumarin*,  $\text{OEt}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{CHBr}\cdot\text{CHPh} \\ \text{CO}-\text{O} \end{smallmatrix}$ , prepared by the action of bromine on ethoxystilbenecarboxylic acid, crystallises from absolute alcohol in colourless needles and melts at  $103^{\circ}$ .

6- (or 7-) *Ethoxy-3-phenylisocoumarin*,  $\text{OEt}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{CH}\cdot\text{CPh} \\ \text{CO}-\text{O} \end{smallmatrix}$ , prepared

by distilling the preceding compound, separates from alcohol in large, flat crystals and melts at  $144-145^{\circ}$ . 4'- (or 5'-) *Ethoxydeoxybenzoïn-2'-carboxylic acid*,  $\text{OEt}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{COPh}$ , prepared by the action of potassium hydroxide on the preceding compound, crystallises from dilute alcohol in long, silky needles and melts at  $172-173^{\circ}$ ; with hydroxylamine, it gives the *oximic acid*,  $\text{OEt}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CPh}\cdot\text{NOH}$ , which separates from dilute alcohol in small, pale rose-coloured, pointed crystals, and melts and intumesces at  $174^{\circ}$ ; when this is allowed to cool after fusion and crystallised from

acetic acid, the *oximinolactone*,  $\text{OEt}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{CH}-\text{CPh} \\ \text{CO}\cdot\text{O}\cdot\text{N} \end{smallmatrix}$ , is obtained in

clear, rhombic tablets melting at  $164.5-166^{\circ}$ . The *phenylhydrazone*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CPh}\cdot\text{N}_2\text{HPh}$ , prepared by the action of phenylhydrazine on the ketonic acid, separates from alcohol in white, felted flakes and melts at  $187^{\circ}$ . 6-(or 7-) *Ethoxy-3-phenyldihydroisocoumarin*,

$\text{OEt}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{CH}_2\cdot\text{CHPh} \\ \text{CO}-\text{O} \end{smallmatrix}$ , prepared by reducing the ketonic acid with

sodium amalgam, crystallises from dilute alcohol in microscopic tablets and melts at  $83-84^{\circ}$ ; by heating the crude alkaline solution obtained on reduction, the isomeric  $\beta$ -ethoxystilbenecarboxylic acid is formed, as in the case of the isomeride described above. 6-(or 7-) *Ethoxy-3-*

*phenylisocarbostyryl*,  $\text{OEt}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{CH}\cdot\text{CPh} \\ \text{CO}-\text{NH} \end{smallmatrix}$ , prepared by the action of

ammonia on ethoxyphenylisocoumarin, forms minute, pointed crystals and melts at  $161^{\circ}$ . 1-Chloro-6-(or 7-) *ethoxy-3-phenylisoquinoline*,

$\text{OEt}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{CH}\cdot\text{CPh} \\ \text{CCl}\cdot\text{N} \end{smallmatrix}$ , prepared by the action of phosphorus oxy-

chloride on ethoxyphenylisocarbostyryl, crystallises from hot alcohol in pointed prisms and melts at  $113-114^{\circ}$ . 1-Iodo-6-(or 7-) *hydroxy-3-*

*phenylisoquinoline*,  $\text{OH}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{CH}\cdot\text{CPh} \\ \text{CI}=\text{N} \end{smallmatrix}$ , prepared by the action of

hydriodic acid and phosphorus on the preceding compound, forms yellowish, pointed crystals and melts at  $141-143^{\circ}$ ; by the further action of hydriodic acid and phosphorus, the *hydriodide* of 6-(or 7-)

*hydroxy-3-phenylisoquinoline*,  $\text{OH}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{CH}\cdot\text{CPh} \\ \text{CH}\cdot\text{N} \end{smallmatrix}$ , is obtained in

yellow, microscopic needles which darken at  $180^{\circ}$ , become deep brown-red at  $190^{\circ}$ , sinter at  $196^{\circ}$ , and melt and decompose at  $203-204^{\circ}$ ;

the *base* crystallises from a mixture of alcohol and light petroleum in microscopic, felted prisms, which sinter at 190—191° and melt at 196—197° to a yellowish-brown liquid; the *hydrochloride* forms long, silky prisms; the *platinichloride* separates from alcohol in golden-yellow needles, sinters at 253°, and melts at 267—269°; the *picrate* crystallises in long, yellow needles and melts at 211—212°.

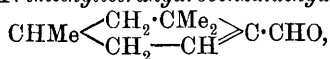
*α-Aminophthalic acid*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{H})_2$ , is a yellow, crystalline powder, dissolves readily in acids and alkalis, darkens at 174°, sinters at 179—181°, and melts at 184—186° with liberation of carbon dioxide; the *copper* salt crystallises in small, green, sparingly soluble tablets. *Methyl α-methoxyphthalate*,  $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{Me})_2$ , crystallises from hot water in small needles and melts at 71°. T. M. L.

**Ethereal Carbonyldiphenylglycinates.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 121198).—*Ethyl carbonyldiphenylglycinate*,  $\text{CO}(\text{NPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et})_2$ , prepared by passing carbonyl chloride through melted ethyl phenylglycinate, is separated from the soluble hydrochloride of the unaltered ester by treatment with water; it melts at 57°. The corresponding *methyl* ester is obtained in a similar manner. These substances are readily converted into indigotin (compare Abstr., 1901, i, 714). G. T. M.

**Artemisin.** By MARTIN FREUND and LUDWIG MAI (*Ber.*, 1901, 34, 3717—3719).—As a lactone, artemisin dissolves in dilute aqueous barium hydroxide, and on adding silver nitrate to a solution of the soluble barium salt so formed, the *silver* salt,  $\text{C}_{15}\text{H}_{19}\text{O}_5\text{Ag} \cdot 2\text{H}_2\text{O}$ , is precipitated; the derived *methyl* ester,  $\text{C}_{16}\text{H}_{22}\text{O}_5$ , crystallises from alcohol and melts and decomposes at 180°. On distilling artemisin with zinc dust, a *dimethylnaphthalene* boiling at 264° is formed, which is not identical with that obtained by Cannizzaro from *santonin*, as its *picrate* melts at 119°, not at 139°; it is perhaps identical with the  $\beta$ -dimethylnaphthalene of Emmert and Reingruber (b. p. 264°, *picrate* m. p. 118°, Abstr., 1882, 733). W. A. D.

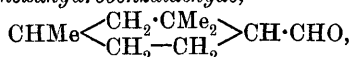
**So called Basic Bismuth Gallate of the Codex.** By PAUL THIBAUT (*J. Pharm. Chim.*, 1901, [vi], 14, 487—493. Compare Abstr., 1893, i, 643; 1901, ii, 106).—An excess of crystallised gallic acid is added to pure hydrated bismuth oxide (the anhydrous oxide has no action) previously mixed with water, and the mixture is well stirred. The action is complete at the end of 24 hours, and the product, after being washed and dried, is amorphous and opaque, and has the composition  $\text{C}_7\text{H}_7\text{O}_7\text{Bi}$ . If the mixture is left for a fortnight, the bismuth compound appears in the form of small, yellow, micaceous crystals, which have the same composition as the amorphous compound. Sulphuric acid diluted to a fifth dissolves this compound in the cold, but when diluted to a tenth only dissolves it when heated. It dissolves in a solution of potassium hydroxide, and the residue left after evaporation and removal of the excess of potassium hydroxide is of definite composition and corresponds with the formula  $\text{K}_2\text{BiC}_7\text{H}_7\text{O}_7 \cdot 2\text{H}_2\text{O}$ . From a consideration of the properties of this potassium salt, the so-called basic bismuth gallate must be regarded, not as a bismuth salt, but as a bismuthigallic acid. The action of sodium hydroxide is similar to that of potassium hydroxide. H. R. LE S.

**Preparation of Hydrogenised Cyclic Aldehydes.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 121975. Compare Abstr., 1900, i, 691, 692).—*Trimethyltetrahydrobenzaldehyde*,



produced by oxidising trimethyltetrahydrobenzylamine with chromic acid mixture in boiling aqueous solution, is a colourless oil volatile in steam and boiling at 90—91° under 18 mm. pressure; it is isomeric with *cyclocitral*; its odour when concentrated resembles that of cedar wood, but when diluted recalls that of violets.

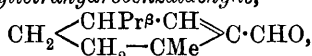
2 : 2 : 4-*Trimethylhexahydrobenzaldehyde*,



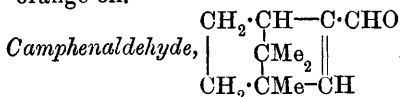
prepared in a similar manner from trimethylhexahydrobenzylamine, is a colourless, pungent oil.

2-*Methyl-5-isopropylhexahydrobenzaldehyde*, derived either from methylisopropylhexahydrobenzylethylamine or methylisopropylhexahydrobenzylamine, is a colourless, pungent oil, which, when diluted, has the odour of geranium oil.

2-*Methyl-5-isopropyltetrahydrobenzaldehyde*,



obtained from 2-methyl-5-isopropyltetrahydrobenzylideneaniline, is a colourless oil boiling at 98° under 15 mm. pressure and has an odour of orange oil.



, produced from the corresponding amine,  $\text{C}_{16}\text{H}_{15}\cdot\text{NHPh}$ , is a colourless pungent oil boiling at 104—105° under 15 mm. pressure. G. T. M.

**Acetates derived from the Aromatic Aldehydes.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 121788).—Aromatic compounds containing methyl groups are oxidised to aldehydes by chromic acid or its salts in the presence of acetic anhydride, the products being shielded from further oxidation by conversion into the corresponding acetyl esters.

*p*-*Nitrobenzylidene diacetate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OAc})_2$ , results from the action of chromic acid on a cold solution of *p*-nitrotoluene, sulphuric acid, acetic anhydride, and acetic acid; it crystallises from alcohol in truncated prisms and melts at 125°. The corresponding *diacetate* from *o*-nitrotoluene melts at 87—88°.

The *tetra-acetate*,  $\text{C}_6\text{H}_4[\text{CH}(\text{OAc})_2]_2$ , derived from *isophthalaldehyde* and produced by the oxidation of *m*-xylene by the preceding method, separates in needles melting at 101°. The *tetra-acetates* derived from *o*- and *p*-xylene melt respectively at 126—127° and 164—165°. These acetates on hydrolysis yield the corresponding aldehydes. G. T. M.

**New Aromatic Aldehyde occurring in Eucalyptus Oils.** By HENRY G. SMITH (*J. Roy. Soc. N.S. Wales*, 1900, 286—295).—The crude oil of *Eucalyptus hemiphloia* was distilled; after the con-



stituents boiling below  $190^{\circ}$  had been removed, the residue, on treatment with sodium hydrogen sulphite, yielded a crystalline mass which, when decomposed with sodium carbonate, furnished an aldehyde. This aldehyde (*aromadendral*),  $C_{10}H_{14}O$ , boils at  $210^{\circ}$ , has a yellowish colour, a sp. gr.  $0.9477$  at  $15^{\circ}/15^{\circ}$ , and  $[\alpha]_D - 49.19$ ; it can also be obtained from the higher boiling fractions of the oils of *E. cnerioifolia*, *E. albens*, and *E. Woolsiana*. Its *oxime* forms colourless crystals and melts at  $84^{\circ}$ . The *phenylhydrazone* melts and decomposes at  $105^{\circ}$ . The  $\beta$ -naphthacinchonic acid melts and decomposes at  $247^{\circ}$ . When the aldehyde is oxidised with potassium dichromate, crystals of *aromadendric acid*,  $C_9H_{13}\cdot CO_2H$ , are obtained; it melts at  $110^{\circ}$ , is soluble in alcohol, ether, or hot water, and furnishes *ammonium*, *silver*, and *copper* salts. If the aldehyde is oxidised with potassium permanganate, eucalyptol is produced, together with an acid which is easily soluble in alcohol or ether, melts at  $259$ – $260^{\circ}$ , and is thereby converted into the anhydride. This *anhydride* melts at  $152^{\circ}$ , sublimes readily, and is very soluble in alcohol, ether, or boiling water. E. G.

**Dialdehydes resulting from Aldehydes and Aromatic Hydroxyaldehydes. I. Action of Benzaldehyde on Vanillin.** By M. ROGOFF (*Ber.*, 1901, 34, 3881–3884).—*Benzylidenedivanillin*,  $CHPh[C_6H_4(OMe)(OH)\cdot CHO]_2$ , prepared by condensing benzaldehyde with vanillin in presence of zinc chloride, forms white, microscopic needles, melts at  $221.5$ – $222.5^{\circ}$  (corr.) to a reddish-brown liquid, reduces ammoniacal silver solution in the cold and Fehling's solution on warming, dissolves in sodium hydroxide, ammonia, and sodium carbonate, but not in sodium hydrogen carbonate, and is readily soluble in most organic solvents, but only sparingly so in benzene or ether, and not at all in light petroleum. The *hexa-acetate*,  $C_{35}H_{16}O_{14}$ , prepared by the action of acetic anhydride and sulphuric acid on the preceding compound, crystallises from 60 per cent. alcohol, melts at  $159.5$ – $162.5^{\circ}$  (corr.), and is not hydrolysed by heating for 10 minutes with 15 per cent. sodium hydroxide. T. M. L.

**[Oxidation of Mesityl Methyl Ketone and  $\psi$ -Cumyl Methyl Ketone].** By L. VAN SCHERPENZEEL (*Rec. Trav. Chim.*, 1901, [ii], 20, 328–330).—In a previous paper (*Abstr.*, 1901, i, 328), the author made no mention of the isolation by Meyer and Molz (*Abstr.*, 1897, i, 474) of mesitylglycollic acid during the oxidation of mesityl methyl ketone.

$\psi$ -Cumyl methyl ketone, which melts at  $11^{\circ}$  and boils at  $245$ – $250^{\circ}$ , gives, on oxidation with potassium permanganate at  $15^{\circ}$ , according to Claus' method (*Abstr.*, 1890, 981),  $\psi$ -cumylglyoxylic acid without any  $\psi$ -cumylglycollic acid; the acid obtained melted at  $61$ – $62^{\circ}$  and the melting point could not be raised to  $75^{\circ}$ , that given by other authors.

W. A. D.

**Two Stereoisomeric Benzylidenedeoxybenzoin.** By HANS STOBBE and KARL NIEDENZU (*Ber.*, 1901, 34, 3897–3913).—When a mixture of deoxybenzoin and benzaldehyde in mol. proportion is saturated with hydrogen chloride, according to Klages and Knoevenagel's method (*Abstr.*, 1893, i, 350, 353), besides chlorobenzyldeoxybenzoin

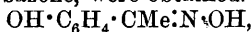
(which melts at  $172-172.5^\circ$  and not at  $182-185^\circ$ ), benzamarone (m. p.  $215-216^\circ$ ) and a ketone, *isobenzylidenedeoxybenzoin* (phenyl  $\alpha$ -phenylcinnamyl ketone),  $\text{CHPh}:\text{CPh}\cdot\text{COPh}$  (m. p.  $88-89^\circ$ ), are formed. The latter is stereoisomeric with benzylidenedeoxybenzoin, formed by the action of concentrated alkali hydroxides on the chloro-compound just mentioned (compare Klages and Knoevenagel) and identical with the ketone,  $\beta\text{-C}_{21}\text{H}_{16}\text{O}$ , obtained by distilling benzamarone (Klingemann, Abstr., 1893, i, 353); it is formed to the extent of 60—70 per cent. when hydrogen chloride is passed into a mixture of deoxybenzoin (2 mols.) and benzaldehyde (1 mol.) at a temperature of  $75-80^\circ$ , and crystallises in yellow prisms or white needles. It is distinguished from its isomeride by the fact that it dissolves in sulphuric acid with a purple-red colour, which in a few seconds becomes violet, and, later, dark green; addition of water produces an orange-red coloration; benzylidenedeoxybenzoin, on the other hand, dissolves in sulphuric acid with an orange-red coloration which does not change; on addition of water, the solution becomes colourless. After prolonged heating with phenylhydrazine, the *iso* compound yields the phenylhydrazone of benzylidenedeoxybenzoin (m. p.  $163-164^\circ$ ). On oxidation with nitric acid, both substances yield benzoic acid and benzil (or their nitro-derivatives). By heating either of the ketones alone at  $160^\circ$ , or by boiling or by exposing to light a solution of either in benzene in the presence of iodine, a mixture of the two ketones is always obtained, partial transformation of the one into the other having taken place. With bromine, *isobenzylidenedeoxybenzoin* gives the same dibromo-compound (m. p.  $134-135^\circ$ ) as does benzylidenedeoxybenzoin. With deoxybenzoin, the normal reacts far more readily than the *iso*-compound to form benzamarone.

On treating the normal ketone in benzene solution with hydrogen chloride, chlorobenzyldeoxybenzoin (m. p.  $172^\circ$ ) and the *isoketone* are formed; similarly, the *isoketone* yields, but more slowly, the same chloro-compound, together with a certain amount of the normal ketone. The chloro-compound (m. p.  $135^\circ$ ) obtained by Klingemann (*loc. cit.*) was not found.

From these facts, the conclusion is drawn that under the action of hydrogen chloride, benzaldehyde and deoxybenzoin first form *isobenzylidenedeoxybenzoin*, which is transformed into the normal ketone; the latter then combines with hydrogen chloride, forming chlorobenzyldeoxybenzoin.

K. J. P. O.

**Constitution of Piceol.** By ERNEST CHARON and DÉMÉTRIUS ZAMANOS (*Compt. rend.*, 1901, 133, 741—743. Compare Tanret, Abstr., 1894, i, 616).—It is shown that piceol (obtained from a glucoside, picein, occurring in the leaves of *Pinus picea*) is *p*-hydroxyacetophenone. From piceol and synthetical *p*-hydroxyacetophenone, the same oxime, phenylhydrazone, and semicarbazone, were obtained. The *oxime*,



crystallises in colourless needles melting at  $143^\circ$ ; the phenylhydrazone melts at  $148^\circ$ ; the *semicarbazone* crystallises in colourless needles and melts at  $199^\circ$ .

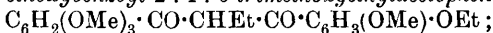
The authors have prepared *p*-hydroxyacetophenone from anisole; this is first converted into *p*-methoxyacetophenone by the action of acetyl

chloride and aluminium chloride, and the methoxy-group in the latter is then converted into hydroxyl by passing hydrogen bromide into hot water containing the *p*-methoxyacetophenone in suspension.

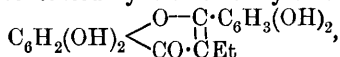
K. J. P. O.

**$\alpha$ -Hydroxybenzylideneacetophenone.** By F. J. POND, H. J. YORK, and B. L. MOORE (*J. Amer. Chem. Soc.*, 1901, 23, 789—796. Compare Abstr., 1900, i, 102).—When bromine is added to an ethereal solution of benzylideneacetophenone, a dibromide separates which melts at 157° (Wislicenus, Abstr., 1900, i, 37); by evaporating the filtrate, a second (or  $\beta$ -) *dibromide* is obtained, which crystallises in small, slender needles and melts at 108—109°. If the  $\alpha$ -dibromide (1 mol.) is heated with sodium methoxide (2 mols.), the *methyl ether* of  $\alpha$ -hydroxybenzylideneacetophenone is produced as an oil which boils at 206—210° under 12 mm. pressure, and is readily hydrolysed by hydrochloric acid with formation of the  $\alpha$ -hydroxy-compound. The *ethyl ether* may be prepared in a similar manner. The  $\alpha$ -hydroxybenzylideneacetophenone, obtained as above, is identical with that described by Wislicenus (*loc. cit.*), but the isomeric dibenzoylmethane is not produced under these conditions. The *copper* and *iron* salts are described. E. G.

**$\alpha$ -Ethylluteolin.** By STANISLAUS VON KOSTANECKI and A. RÓŻYCKI (*Ber.*, 1901, 34, 3719—3721. Compare Kostanecki and Lloyd, Abstr., 1901, i, 735).—2 : 4 : 6 : 3'-Tetramethoxy-4'-ethoxybenzoylacetophenone (Diller and Kostanecki, Abstr., 1901, i, 476) interacts with ethyl iodide in boiling alcoholic potassium hydroxide solution to form 3'-methoxy-4'-ethoxybenzoyl-2 : 4 : 6-trimethoxyethylacetophenone,



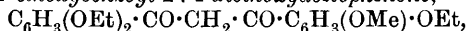
this crystallises from alcohol in white leaflets, melts at 132—133°, and when boiled with concentrated hydriodic acid yields  $\alpha$ -ethylluteolin,



which crystallises from dilute alcohol in pale yellow needles, melts at 286—287°, and yields a *tetra-acetyl* derivative crystallising in white needles and melting at 129—130°. W. A. D.

**3 : 3' : 4'-Trihydroxyflavone.** By STANISLAUS VON KOSTANECKI and A. RÓŻYCKI (*Ber.*, 1901, 34, 3721—3727).—Previous attempts to prepare this substance have failed (Emilewicz and Kostanecki, Abstr., 1899, i, 368, and Kostanecki and Różycki, *ibid.*, i, 911), but the following method gave the desired result.

3'-Methoxy-4'-ethoxybenzoyl-2 : 4-diethoxyacetophenone,



which is obtained by heating ethyl ethylvanillate with resacetophenone diethyl ether in presence of sodium, crystallises from alcohol in yellow needles, melts at 134—135°, and with boiling hydriodic acid yields

3 : 3' : 4'-trihydroxyflavone,  $\text{OH} \cdot \text{C}_6\text{H}_3 \begin{array}{l} \text{O} - \text{C} \cdot \text{C}_6\text{H}_3(\text{OH})_2 \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{CH} \quad \text{CO} \cdot \text{CH} \end{array}$ ; the latter

crystallises from very dilute alcohol in slightly yellow needles, melts at 326—327°, and yields a *tri-acetyl* derivative crystallising in white needles and melting at 209—210°.

*Benzoyl-2:4-diethoxyacetophenone*,  $C_6H_5(OEt)_2 \cdot CO \cdot CH_2Bz$ , obtained by condensing ethyl benzoate and resacetophenone diethyl ether with sodium, crystallises from alcohol in yellow needles, melts at  $120-121^\circ$ , and is converted by boiling hydriodic acid into 3-ethoxyflavone.

W. A. D.

**Addition of Alcohols to Quinone.** By EMIL KNOEVENAGEL and CARL BÜCKEL (*Ber.*, 1901, **34**, 3993—3998).—When ethyl alcohol is heated with quinone in the presence of zinc chloride, an interaction takes place in which *p*-diethoxyquinone (compare Nietzki and Recheberg, *Abstr.*, 1890, i, 967) and quinol are formed quantitatively. Other primary alcohols (ethyl alcohol, &c.) behave in an analogous manner. In the absence of zinc chloride, no such reaction takes place; other metallic chlorides cannot be substituted for zinc chloride. *2:5-Dibenzoyloxyquinone*,  $C_6H_2O_2(OBz)_2$ , prepared by heating with benzoyl chloride the *p*-dihydroxyquinone obtained from diethoxyquinone, crystallises in yellow leaflets melting at  $174^\circ$ . *2:5-Dipropoxyloxyquinone*,  $C_6H_2O_2(OPr^a)_2$ , crystallises in golden-yellow leaflets melting at  $187^\circ$ . *2:5-Dipropoxyloxyquinol*,  $C_6H_2(OH)_2(OPr^a)_2$ , prepared by reducing with stannous chloride the corresponding quinone, crystallises in flattened needles melting at  $95^\circ$ .

K. J. P. O.

**Attempted Synthesis of the Camphor Ring as a Contribution to the Tension Theory.** By NICOLAI D. ZELINSKY (*Ber.*, 1901, **34**, 3798—3801).—The author has attempted to convert the *cis-trans*-form of hexahydroterephthalic acid into a dicyclic ketone, that is, a compound containing the camphor ring. On heating the barium salt of the acid with calcium carbonate, hydrogen is evolved and benzene obtained, together with a small quantity of a substance of a ketonic nature. This substance yielded a *semicarbazone*,  $C_8H_{13}ON_3$ , which crystallised in white scales melting at  $209-210^\circ$  and is probably the derivative of a dicyclic heptanone.

K. J. P. O.

**Action of Cyanogen Chloride on Sodium Camphor.** By H. DUVAL (*Bull. Soc. Chim.*, 1901, [iii], **25**, 953—955).—By the action of cyanogen chloride on sodium camphor, a compound,  $C_{12}H_{16}O_2N_2$ , was obtained; this crystallises from hot water (which dissolves about 9 grams per litre) in colourless needles, melts at  $168^\circ$ , and has acid properties. It is regarded as a product of hydrolysis of dicyanocamphor,  $C_8H_{14} \begin{smallmatrix} < C(CN)_2 \\ CO \end{smallmatrix} \rightarrow C_8H_{14} \begin{smallmatrix} < CH(CN)_2 \\ CO_2H \end{smallmatrix}$ .

T. M. L.

**Transformation and Oxidation of Fenchoneimine by Atmospheric Oxidation.** By FRIEDRICH MAHLA (*Ber.*, 1901, **34**, 3777—3785. Compare *Abstr.*, 1897, i, 85).—Fenchoneimine,  $CH_2 \cdot \overset{\text{CHMe}}{\underset{|}{C}} \cdot CHMe$

$\left| \begin{array}{c} CMe_2 \\ | \end{array} \right|$ , obtained by treating fenchonenitrimine with 25 per cent. ammonia, boils at  $83^\circ$  under 15 mm. pressure, has  $[a]_D 76.30^\circ$  at  $19.5^\circ$ , a sp. gr. 0.9322 at  $11.5^\circ$ , and  $n_D 1.47809$  at  $17^\circ$ ; the experi-

mental and calculated values for the molecular refraction are 45.857 and 45.78 respectively. The anhydrous base is stable and remains unchanged even when heated at 200°. The *picrate*,  $C_{16}H_{20}O_7N_4$ , melts at 202°; *methylfenchoneimine iodide*,  $C_{11}H_{20}NI$ , is a crystalline product formed from methyl iodide and fenchoneimine dissolved in anhydrous ether. When a stream of dry air is passed through fenchoneimine heated at 105°, the base is partly transformed into *dihydrofenchonitrile*,  $\begin{array}{c} CH_2 \cdot CMe_2 \\ | \\ CH_2-CH_2 \end{array} > CH \cdot CHMe \cdot CN$ , and partly oxidised to *hydroxydihydro-*

*fenchonitrile*,  $\begin{array}{c} CH_2-CH_2 \\ | \\ OH \cdot CH \cdot CMe_2 \end{array} > CH \cdot CHMe \cdot CN$ ; the former compound is an oil boiling at 98—104° and having a pungent odour recalling that of fenchonitrile; it has  $n_D$  1.44743 at 17.5°; the experimental mol. refraction is 45.15°, the calculated value being 45.09. This nitrile, when hydrolysed with boiling 30 per cent. alcoholic potassium hydroxide solution, is only partially decomposed, yielding a mixture of *dihydrofencholenamide* and *dihydrofencholenic acid*,  $\begin{array}{c} CH_2 \cdot CMe_2 \\ | \\ CH_2-CH_2 \end{array} > CH \cdot CHMe \cdot CO_2H$ , the latter in the form of its potassium salt. The amide melts at 130.5° and sublimes slowly at 107°; it is only incompletely hydrolysed by alcoholic potassium hydroxide solution, but when heated at 200° with concentrated hydrochloric acid yields the corresponding carboxy-acid in theoretical quantities. The acid boils at 145—146° under 13 mm. pressure, and has a sp. gr. 0.9816 at 15° and  $[\alpha]_D$  4.3° at 15.5°.

The *silver* salt crystallises from hot water, the ammonium salt is unstable and hygroscopic.

Hydroxydihydrofenchonitrile, which remains in the residue after distilling the oxidation product of fenchimine in a current of steam, is an oil boiling at 153—154° under 23 mm. pressure; it has a sp. gr. 0.9792 at 15°,  $[\alpha]_D$  -8° at 18°,  $n_D$  1.46464 at 18°, and mol. refraction 47.11, the calculated value of the last constant being 47.30.

*Hydroxydihydrofencholenamide*,  $\begin{array}{c} CH_2-CH_2 \\ | \\ OH \cdot CH \cdot CMe_2 \end{array} > CH \cdot CHMe \cdot CO \cdot NH_2$ , obtained by hydrolysing the preceding nitrile with alcoholic potassium hydroxide solution, crystallises from ethyl acetate and melts at 78°.

*Dihydrofencholenic lactam*,  $\begin{array}{c} CH_2 \cdot CH-CHMe \\ | \quad | \\ CMe_2 \quad CO \\ | \\ CH_2 \cdot CH-NH \end{array}$ , is produced together

with a non-basic, oily substance by dissolving the preceding amide in warm dilute hydrochloric acid; it separates from aqueous solutions in lustrous, highly refractive crystals and melts at 136—137°. It is identical with Wallach's  $\beta$ -fenchoneisooxime obtained from fencholenamide.

*4-Hydroxydihydrofencholenic acid*,  $\begin{array}{c} CH_2-CH_2 \\ | \\ OH \cdot CH \cdot CMe_2 \end{array} > CH \cdot CHMe \cdot CO_2H$ , the ultimate product of the hydrolysis of hydroxydihydrofencholenonitrile, separates from water or ethyl acetate in hard crystals and melts at 113—114°. When heated with water, the acid readily passes

into the lactone,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH} - \text{CHMe} \\ | \quad \quad | \\ \text{CMe}_2 \quad \text{CO} \\ | \quad \quad | \\ \text{CH}_2 \cdot \text{CH} - \text{O} \end{array}$  ; this substance is volatile in steam

and distils alone at 130—150° under 10 mm. pressure, yielding a distillate which solidifies on cooling; it separates from ethyl acetate in well-defined crystals melting at 72°. The lactone is insoluble in sodium carbonate solution, but slowly dissolves in solutions of the alkali hydroxides.

G. T. M.

#### Characterisation and Classification of the Sesquiterpenes.

IV. By OSWALD SCHREINER and EDWARD KREMERS (*Pharm. Arch.*, 1901, 4, 141—165).—The classification of the terpenes generally is discussed at length.

Oil of ginger was distilled under 30 mm. pressure. The first fraction, boiling below 150°, was redistilled under 32 mm. pressure; the portion collected between 80° and 100° yielded a small quantity of a nitrosite which melts at 105° and is probably not phellandrene nitrite as was supposed by Bertram and Walbaum (*Abstr.*, 1894, i, 201). The second fraction (150—162°) consisted chiefly of zingiberene (Soden and Rojahn, *Abstr.*, 1900, i, 605), which boils at 160—161° under 32 mm. pressure, has a sp. gr. 0.8731 at 20°,  $n_D^{20}$  1.49399, and  $[\alpha]_D - 73.38^\circ$ . Its hydrochloride is a white, crystalline substance which melts at 168—169°. The *nitrosite* crystallises in silky needles, melts at 97—98°, and is very unstable. The *nitrosate* is a slightly yellow powder which melts and decomposes at 86—88°. The *nitroschloride* is a white powder which melts and decomposes at 96—97°.

Caryophyllene hydrochloride (*Abstr.*, 1900, i, 106) is a di-derivative. The sesquiterpene obtained by the action of glacial acetic acid and sodium acetate on it, has a sp. gr. 0.9030 at 20°,  $n_D$  1.49976, and  $[\alpha]_D - 8.96^\circ$ , and is neither regenerated caryophyllene nor clovene.

E. G.

**Specific Gravities and Coefficients of Expansion of the Volatile Oils.** By OSWALD SCHREINER and W. R. DOWNER (*Pharm. Arch.*, 1901, 4, 165—173).—The sp. gr. of a large number of volatile oils was determined at 15°/15°, 20°/20°, and 25°/25°. The results show that the change in sp. gr. for each degree is comparatively small, and for any one oil is nearly uniform between 15° and 25°, and not very different for different oils. The average change for each degree is 0.00064; this figure applies fairly accurately to all the oils examined with the exception of those of cade and wintergreen. The data obtained have been employed for the calculation of the coefficients of expansion of the oils between 15° and 25°.

E. G.

**Constituent of Peppermint-like Odour occurring in many Eucalyptus Oils.** By HENRY G. SMITH (*J. Roy. Soc. N. S. Wales*, 1900, 136—142).—The oil of *Eucalyptus dives*, on fractional distillation, yielded 2 per cent. below 172°, 60 per cent. at 172—200°, 13 per cent. at 200—227°, and 20 per cent. at 227—240°. The last fraction, when treated with sodium hydrogen sulphite, furnished a crystalline com-

pound which, on decomposition with sodium hydroxide, yielded a colourless oil of strong peppermint-like taste and odour; this oil is soluble in the usual organic solvents and slightly soluble in water, boils at 224—225°, has a sp. gr. 0.9393 at 17°/15°,  $[\alpha]_D - 0.35^\circ$  (probably due to the presence of a minute quantity of an aldehyde), and the molecular weight 154. By the action of sodium on an alcoholic solution, a reduction product was obtained which crystallises in colourless needles, melts at 155—156°, and is readily soluble in chloroform and slightly so in alcohol, ether, or ethyl acetate.

The fraction of this oil boiling at 227—240° yielded, on hydrolysis, a small quantity of an aromatic alcohol. E. G.

**Amyl Eudesmate occurring in Eucalyptus Oils.** By HENRY G. SMITH (*J. Roy. Soc. N.S. Wales*, 1900, 72—81).—The oil of *Eucalyptus aggregata* yielded on fractional distillation 26 per cent. boiling at 156—164°, which consisted chiefly of *d*-pinene; 12 per cent. was obtained between 164° and 245°, and 22 per cent. between 245° and 292°; the residue, on cooling, became partly crystalline. Phellandrene and eucalyptol could not be detected. When the oil is hydrolysed with potassium hydroxide, amyl alcohol is produced. If the fraction boiling at 245—292° is shaken with aqueous potassium hydroxide and the alkaline solution acidified with hydrochloric acid, eudesmic acid,  $C_{13}H_{17}CO_2H$ , separates, which crystallises in rhombic prisms, melts at 160° (uncorr.), is soluble to the extent of 0.0738 per cent. in water at 20°, and readily so in hot water, alcohol, ether, acetone, or chloroform; it sublimes at a high temperature without decomposition. Its ammonium, ferric, copper, and silver salts are described. The bromide,  $C_{14}H_{18}O_2Br_2$ , forms colourless crystals and melts at 102—103°. By the action of nitric acid on eudesmic acid, a substance is obtained which crystallises in microscopic needles, melts at 113°, and is probably cumic acid.

The amount of amyl eudesmate present in the oil is 57.7 per cent.

E. G.

**Oriental Storax.** By ALEXANDER TSCHIRCH and LEOPOLD VAN ITALLIE (*Arch. Pharm.*, 1901, 239, 506—532).—This is a secretion which forms slowly when incisions are made through the bark of *Liquidambar orientalis* into the wood. It is almost entirely soluble in ether; the residue appears to contain vanillin and also a phlobaphen, since it yields phenol, acetic acid, phloroglucinol and protocatechuic acid when fused with potash. Styrene is present ready formed in the balsam.

From an ethereal solution of the balsam, 0.1 per cent. aqueous sodium carbonate extracts cinnamic acid. Saturated sodium hydrogen sulphite solution then extracts vanillin, which could not be obtained pure, however. Finally, 1 per cent. aqueous sodium hydroxide extracts a resin, at the same time hydrolysing a portion of the latter with formation of a gelatinous mass. In the ethereal solution a mixture of ethyl, phenylpropyl and cinnamyl cinnamates remains.

The resin is hydrolysed by prolonged boiling with aqueous sodium hydroxide to cinnamic acid and a resinol, storesinol; no tannol could be detected. Storesinol,  $C_{16}H_{26}O_2$ , melts at 156—161° when quite pure

and dry, otherwise at 93—96°, and is isomeric with benzoresinol (Tschirch and Ludy, Abstr., 1893, i, 480, 1666). It is optically active, with  $[\alpha]_D$  13°3' and 13°32' in 1 and 2·5 per cent. alcoholic solutions respectively; it gives an absorption band between  $\lambda = 0\cdot510$  and  $0\cdot540\mu$ . It forms a crystalline potassium derivative and also a *methyl ether*,  $C_{16}H_{25}O_2Me$ , when its concentrated methyl alcoholic solution is boiled for a long time with methyl iodide; it does not form an acetyl or benzoyl derivative, neither will it react with hydroxylamine or phenylhydrazine; it contains no methoxyl or ethoxyl group. When it is mixed with strong sulphuric acid and the mixture diluted with water after a few minutes and heated to boiling, part of the product is insoluble in ether, but soluble in chloroform and is precipitated from the solution in needles by ether. This substance, styrogenin (Mylius, *Pharm. Centralhalle*, 1882, 79), melts above 360° and has the composition  $C_{26}H_{40}O_3$ . When storesinol is treated with hydrogen bromide in chloroform solution, or heated with 50 per cent. hydrobromic acid in sealed tubes, a *product*,  $C_{16}H_{26}O_3$  is obtained, melting at about 280°; the same product is obtained with hydriodic acid, but in no case is the yield good. When storesinol is brominated in acetic acid solution, hydrogen bromide is evolved and an amorphous product is formed containing a varying amount of bromine. Nitric acid of sp. gr. 1·317 oxidises storesinol to picric and oxalic acids and a substance containing nitrogen; chromic acid oxidises it to benzoic acid, dilute aqueous potassium permanganate at 65—70° to phthalic acid and an *acid* which melts at 199°, is insoluble in water, and requires 10·5 c.c. *N*/10 alkali to neutralise 0·357 gram, with phenolphthalein as indicator. Attempts to reduce storesinol with sodium amalgam and with zinc and acetic acid had no result. Fusion with potassium or sodium hydroxide leads to the formation of acetic and salicylic acids. Dry distillation yields phenol and cresol, with benzene, toluene, and probably phenylacetylene. Distillation with zinc dust yields phenol, with benzene and toluene; no naphthalene is formed.

In 100 parts of a sample of the drug, there were contained: Insoluble in ether, 2·4; free cinnamic acid, 23·1; water, 14; aromatic esters, 22·5; styrene and vanillin, 2·0; resin, 36·0. The acid number was 81·0; the saponification number, 179·0; saponification number of the mixture of esters and styrene, 209·0. About half of the combined cinnamic acid was contained in the resin, the rest in the aromatic esters.

C. F. B.

**American Storax.** By ALEXANDER TSCHIRCH and LEOPOLD VAN ITALLIE (*Arch. Pharm.*, 1901, 239, 532—541).—This substance, also called *sweet gum*, is a secretion which is formed gradually after incisions have been made through the bark of *Liquidambar styraciflua* into the wood. It was examined in the same way as oriental storax (preceding abstract) and found to contain much the same constituents. Of aromatic esters, however, ethyl cinnamate could not be detected with certainty, and the resinol obtained,  $C_{16}H_{26}O_2$ , has  $[\alpha]_D$  52°, although in all other respects it resembles storesinol; it is therefore regarded provisionally as isomeric with this substance, and is named *styresinol*; it is present both in the free state and as a cinnamate.



In 100 parts of the balsam there are contained : Insoluble in ether, 3.12; free cinnamic acid, 23.4; aromatic esters, 25; styrene and vanillin, 2.0; resin, 45.0. The acid number was 89.3; saponification number, 192.7; the saponification number of the mixture of aromatic esters and styrene, 205.1. Rather more than half of the combined cinnamic acid was contained in the aromatic esters, the rest in the resin.

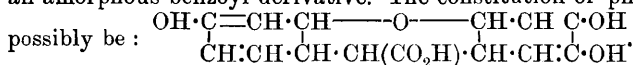
C. F. B.

**Rassamala Resin.** By ALEXANDER TSCHIRCH and LEOPOLD VAN ITALLIE (*Arch. Pharm.*, 1901, 239, 541—547).—This substance, the product of *Altingia excelsa* (Java), has been subjected to a preliminary examination. It contains benzaldehyde, cinnamic acid and cinnamaldehyde, also a resin and a pentosan; esters are not present. The balsam is undoubtedly different from either oriental or American storax, with which it has often been confused.

C. F. B.

**Phoenicein, the Dye from Purple Wood.** By ESTELLA KLEEREKOPER (*Chem. Centr.*, 1901, ii, 1085—1086; from *Ned. Tijds. Pharm.*, 1901, 13, 284—288, 303—314. Compare this vol., i, 48).—Further examination has shown that phoenin is not a glucoside. By heating for a long time at 100°, or for an hour at 150—160°, or by the action of dilute acids, it is converted quantitatively into phoenicein with elimination of 1H<sub>2</sub>O. With alkalis, phoenicein, C<sub>14</sub>H<sub>14</sub>O<sub>6</sub>, gives a blue coloration, which becomes violet and finally brown, the alkali salt first formed being reconverted into phoenin and then undergoing further decomposition.

Phoenicein crystallises in minute rods, begins to darken at about 190°, and is easily soluble in methyl or ethyl alcohol and slightly so in water containing mineral acids. With alkalis and ammonia, it forms unstable blue salts. The red colour of the product obtained by boiling phoenin with hydrochloric acid is due to the presence of an unstable compound of phoenicein with the acid; this compound is decomposed by water, being reconverted into phoenicein. This property of combining with both acids and alkalis is shared by other dyes of the flavone and quercetin groups (compare Perkin, *Trans.*, 1899, 75, 433), and, like these, phoenicein also gives a blue precipitate with sodium acetate in alcoholic solution. When reduced by zinc dust and glacial acetic acid, it forms a leuco-compound, which is very readily oxidised by exposure to the air, and with aluminium hydroxide and ferric hydroxide it forms blue and brown lakes respectively. By the action of acetic anhydride, an acetyl compound, which apparently contains three acetyl groups, is obtained as a yellowish-white powder, and with nitric acid, phoenicein gives trinitroresorcinol and carbon dioxide. Carbon dioxide is also eliminated by dry distillation or by the action of an alkali, a phenol being probably formed in the latter case. When treated with bromine, phoenicein yields substitution derivatives; with sulphuric acid, it gives a sulpho-derivative, and with benzoyl chloride, an amorphous benzoyl derivative. The constitution of phoenicein may possibly be :



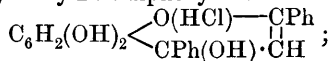
E. W. W.

**Basic Properties of Oxygen.** By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1901, **34**, 3612—3618. Compare *Abstr.*, 1901, i, 658).—Unsaturated hydrocarbons of the ethylene type do not combine with acids. Ferricyanic acid is a strong oxidising agent, and most of the oxonium salts previously described contain small amounts of ferrocyanides. Dimethylpyrone hydrochloride is readily formed when a solution of the base and acid in mol. quantities is evaporated. In concentrated solution, it appears to exist as the salt, but in dilute solution is completely dissociated. As regards basic properties, dimethylpyrone closely resembles carbamide; other oxygen compounds, for example, alcohols and the higher ethers, have basic characteristics analogous to those of nitriles. The latter dissolve in concentrated hydrochloric acid and are thrown down unaltered on dilution. With ferrocyanic, ferricyanic, and cobalticyanic acids, they form crystalline salts. Salts of the following nitriles have been obtained: propionitrile, *n*-butyronitrile, valeronitrile, hexonitrile, and benzonitrile, and benzyl cyanide. J. J. S.

**Oxonium Salts.** By JOHN THEODORE HEWITT (*Ber.*, 1901, **34**, 3819—3822. Compare *Zeit. physikal. Chem.*, 1901, **34**, 1).—As the result of Werner's publication (this vol., i, 50), attention is drawn to the fact that the author had previously (*loc. cit.*) noted attention to the possibility of the existence of quadrivalent oxygen in xanthidrol salts. These salts, and also those of phenyl- $\beta$ -dinaphthoxanthidrol in dilute solution exhibit strong fluorescence. Xanthidrol and picric acid yield a compound,  $C_6H_2(NO_2)_3 \cdot O \cdot O \leq C_6H_4 \rangle CH$ , in the form of dark green, glistening crystals. J. J. S.

**Dihydroxy-derivatives of 2:4-Diphenyl-1:4-benzopyranol.** By CARL BÜLOW and WALTHER VON SICHERER (*Ber.*, 1901, **34**, 3916—3929).—Pyrogallol, phloroglucinol, and hydroxyquinol all condense with dibenzoylmethane, yielding various dihydroxy-2:4-diphenyl-1:4-benzopyranols. These are of a strongly basic nature and the formation of their stable hydrochlorides, sulphates, &c., can only be readily explained by the assumption that the ring oxygen atom is quadrivalent (see also *Abstr.*, 1901, i, 400, 599, and 603).

When a stream of dry hydrogen chloride is passed for eight hours into a solution in glacial acetic acid of pyrogallol and dibenzoylmethane, a mass of violet-brown crystals is obtained consisting of the *hydrochloride* of 7:8-dihydroxy-2:4-diphenyl-1:4-benzopyranol,



this crystallises from alcohol containing a little free hydrogen chloride in claret-coloured, felted needles with a coppery lustre, and loses hydrogen chloride when placed in a vacuum or when treated with sodium acetate, yielding the *base* which crystallises in microscopic, violet needles and dissolves in most solvents except water and light petroleum. The constitution of the base is proved by (a) the formation of a *triacetyl* derivative, which crystallises from pyridine in short, dark brown prisms and decomposes at (about) 230°, and (b) by its

hydrolysis to acetophenone, 1 : 2 : 3-trihydroxybenzophenone, pyrogallol, and benzoic acid. The *picrate* crystallises in small, lustrous, brownish-violet needles, which begin to soften at 200° and to melt and decompose at 242°. The *platinichloride* crystallises in lustrous, copper-coloured, felted needles, which begin to soften at 150° and melt at 178°.

5 : 7-*Dihydroxy-1 : 4-benzopyranol*, prepared by condensing phloroglucinol with dibenzoylmethane, is obtained as small, pinkish, cubical crystals; the *hydrochloride* forms lustrous, red, prismatic crystals, is very slightly soluble in water, alcohol, or acetic acid, and decomposes above 260°; the *triacetyl* derivative crystallises from nitrobenzene in dark brown prisms, which gradually decompose above 200°; the 8-*nitroso*-derivative, obtained when the hydrochloride dissolved in acetic acid is treated with nitrous acid, crystallises in slender, reddish-brown needles and decomposes above 230°.

6 : 7-*Dihydroxy-2 : 4-diphenyl-1 : 4-benzopyranol*, obtained from hydroxyquinol by analogous methods, crystallises from alcohol in ruby-red prisms; the *hydrochloride* crystallises in lustrous, ochre-yellow plates, which, when heated, begin to decompose at 250° and melt and evolve gas at 272°; the *picrate* crystallises in small, red needles, which soften at 220° and melt and decompose at 236°. R. H. P.

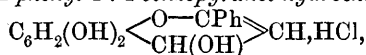
**New Benzopyranol Derivatives from Benzoylacetaldehyde and Polyhydric Phenols.** By CARL BÜLOW and WALTHER VON SICHERER (*Ber.*, 1901, **34**, 3889—3897. Compare *Abstr.*, 1901, i, 400, 559, 603).—7-*Hydroxy-2-phenyl-1 : 4-benzopyranol hydrochloride*,

$\text{OH} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{CPh} \\ \text{CH}(\text{OH}) \end{smallmatrix} \text{CH} \cdot \text{HCl}$ , is formed when a solution in acetic acid of benzoylacetaldehyde and resorcinol in mol. proportion is saturated with dry hydrogen chloride; it forms brownish-orange crystals melting at 152—153°, dissolves in alkalis with a brownish-red colour, and in solution in concentrated sulphuric acid gives an intense green fluorescence. 7-*Hydroxy-2-phenyl-1 : 4-benzopyranol*,  $\text{C}_{15}\text{H}_{12}\text{O}_3$ , prepared by treating an aqueous solution of the hydrochloride with sodium acetate, forms reddish-brown, amorphous flakes; when boiled with aqueous potassium hydroxide it is decomposed into acetophenone, resorcinol, and benzoic acid. The *picrate*,  $\text{C}_{15}\text{H}_{12}\text{O}_3 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , crystallises in dark yellow needles melting and decomposing at 232—234°; the *platinichloride* forms small, orange-yellow scales, which darken at 240° and melt and decompose at 244°; the *aurichloride* crystallises in brownish-yellow needles melting and decomposing at 178°. 7-*Acetoxy-2-phenyl-1 : 4-benzopyranol acetate*,  $\text{C}_{15}\text{H}_{10}\text{O}_3\text{Ac}_2$ , prepared by boiling the hydrochloride with acetic acid and acetic anhydride, forms a violet-grey amorphous powder which begins to melt at 160°. 7-*Methoxy-2-phenyl-1 : 4-benzopyranol*,  $\text{C}_{15}\text{H}_{11}\text{O}_3\text{Me}$ , prepared by treating the hydrochloride with methyl iodide and sodium methoxide, is a brownish-violet, amorphous powder and does not exhibit fluorescence when dissolved in sulphuric acid.

7-*Acetoxy-2-phenyl-1 : 4-dihydrobenzopyran*,  $\text{OAc} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{CHPh} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix}$ , is obtained by reducing the hydrochloride with zinc dust and acetic

acid in presence of acetic anhydride, and is an amorphous powder melting, but not sharply, at 112—114°.

5 : 7-Dihydroxy-2-phenyl-1 : 4-benzopyranol hydrochloride,



prepared by saturating with hydrogen chloride a solution of phloroglucinol and benzoylacetaldehyde, is a brick-red, crystalline powder; the *base* is a brownish-red, amorphous powder.

7 : 8-Dihydroxy-2-phenyl-1 : 4-benzopyranol hydrochloride, prepared from pyrogallol and benzoylacetaldehyde, was obtained only in an amorphous form, and was converted into the *base* by means of sodium acetate; the latter is a dark brown, amorphous powder. K. J. P. O.

**Physiological Properties and Composition of Iboga. Presence of a New Alkaloid, Ibogaine.** By J. DYBOWSKI and EDOUARD LANDRIN (*Compt. rend.*, 1901, 133, 748—750).—Iboga is a plant which grows in French Congo. The woody portions are stated by natives to have an effect when consumed similar to that of alcohol. The active principle, *ibogaine*,  $\text{C}_{52}\text{H}_{66}\text{O}_2\text{N}_6$ , is present in the bark and wood and particularly in the roots of the plant, which yielded 0.6 to 1 per cent. of the alkaloid.

Ibogaine forms long, slightly amber-coloured prisms which melt at 152° and dissolve very readily in alcohol, ether, chloroform, light petroleum, and most other solvents. It is laevorotatory,  $[\alpha]_D - 48.32'$  at 15°. The deviation is 1°56' for 1 gram dissolved in 50 c.c. of alcohol. When exposed to air, ibogaine becomes yellowish-brown and seems to be converted into a non-crystalline substance. Saline solutions are precipitated by Mayer's reagent, by tannin, and by phosphoantimonic acid. Bismuth potassium iodide produces a gold-coloured precipitate. The *sulphate*, *nitrate*, *acetate*, and *benzoate* are neutral, but not crystalline; the *hydrochloride* is crystalline.

As regards the physiological effect of ibogaine, it was found that large doses produce analogous effects to those resulting from excessive consumption of alcohol. N. H. J. M.

**Ipoh Arrow Poisons and some Plants that are used to prepare them.** By C. HARTWICH and P. GEIGER (*Arch. Pharm.*, 1901, 239, 491—506).—A list is given of plants which are used to prepare poisons with which the heads of arrows are smeared; it is noteworthy that such arrows are almost invariably projected from a blowpipe. The chief of these plants are *Antiaris toxicaria*, which contains antiarin; species of *Strychnos*, containing strychnine and brucine; and *Derris elliptica*, which contains derride.

Samples of poison were examined for these substances: antiarin was detected by the golden-yellow coloration, with subsequent fluorescence, which it gives with sulphuric acid, and by the brown coloration with hot aqueous sodium picrate; derride by the blood-red coloration which it gives with sulphuric acid containing a trace of ferric chloride; strychnine by its reaction with vanadosulphuric acid; brucine by its reaction with nitric acid. Of 25 samples, 2 contained derride, 5 brucine, 11 strychnine, and 21 antiarin. With antiarin there is commonly associated a *substance* closely resembling the fluavil

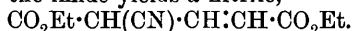
of guttapercha, and also a new alkaloid, *ipohine*, which was found in 12 out of 19 specimens examined. This alkaloid is a virulent poison, causing cessation of the heart's action, much as digitoxin does but a great deal more quickly. Antiarin has a comparatively feeble action.

A morphological description of *Antiaris toxicaria* and *Derris elliptica* is given; also the results of the examination of various Indian species of *Strychnos* for strychnine, brucine, and strychnochromin. The last is detected by the green coloration which it gives with concentrated sulphuric acid and with nitric acid; in its occurrence it seems to bear no relation to strychnine or other alkaloids generally. C. F. B.

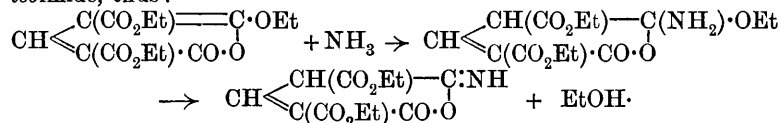
**Conversion of Pyrrole into Pyrroline.** By GIACOMO L. CIAMICIAN (*Ber.*, 1901, **34**, 3952—3955. Compare Knorr and Rabe, this vol., i, 54).—The names  $\Delta^1$ -,  $\Delta^2$ - and  $\Delta^3$ -pyrroline are suggested for the three isomeric compounds,  $N \begin{smallmatrix} \diagup CH-CH_2 \\ \diagdown CH_2 \cdot CH_2 \end{smallmatrix}$ ,  $NH \begin{smallmatrix} \diagup CH:CH \\ \diagdown CH_2 \cdot CH_2 \end{smallmatrix}$ , and

$NH \begin{smallmatrix} \diagup CH_2 \cdot CH \\ \diagdown CH_2 \cdot CH \end{smallmatrix}$ . The compound obtained by the reduction of pyrrole is most probably  $\Delta^3$ -pyrroline, as such a constitution harmonises best with Thiele's theory. The reduction is most economically brought about by the aid of zinc dust and acetic acid, since all unaltered pyrrole can be recovered. When hydrochloric acid is employed, all unreduced pyrrole is resinified. Hielscher's base (*Abstr.*, 1898, i, 338) is 1-methyl- $\Delta^2$ -pyrroline and differs altogether in properties from  $\Delta^3$ -pyrroline. J. J. S.

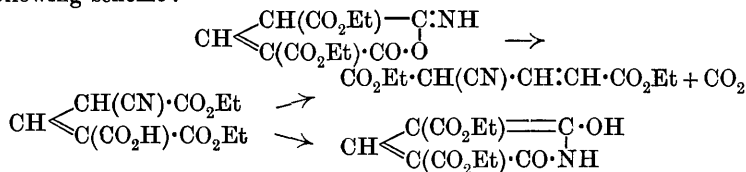
**Desmotropism in the Pyridine Series.** By GIORGIO ERRERA (*Ber.*, 1901, **34**, 3700—3704).—The three modifications of the imide of ethyl dicarboxylglutaconate,  $CH \begin{smallmatrix} \diagup CH(CO_2Et) \cdot CO \\ \diagdown C(CO_2Et) \cdot CO \end{smallmatrix} > NH$ , are probably not desmotropic as considered by Guthzeit (*Abstr.*, 1894, i, 71, and 1895, i, 557), for the change of form is not reversible, and the action of dilute alkalis on the imide yields a nitrile,



In the light of analogous facts (following abstract) the author considers that the action of ammonia on Guthzeit's coumalin derivative gives an isoimide, thus:

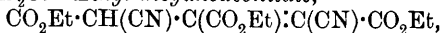


The action of both heat and of alkalis is then explicable by the following scheme:



W. A. D.

**Action of Halogens and of Ethyl Bromocyanoacetate on Ethyl Sodiocyanoacetate.** By GIORGIO ERRERA and F. PERCIABOSCO (*Ber.*, 1901, **34**, 3704—3717. Compare *Abstr.*, 1901, i, 18, and Thorpe and Young, *Trans.*, 1900, **77**, 936).—The action of halogens (iodine in ethereal solution or bromine) on ethyl sodium cyanoacetate gives the same products as the action of ethyl bromocyanoacetate (*loc. cit.*), but the yield is smaller; in addition to ethyl tricyanotrimethylenetricarboxylate (m. p. 119.5°), considerable quantities of *ethyl sodiodicyanoaconitate*,  $\text{CO}_2\text{Et}\cdot\text{CNa}(\text{CN})\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$ , are formed; this separates from alcohol in large, yellow, monoclinic crystals, with  $\frac{1}{2}\text{H}_2\text{O}$ , melts and decomposes at about 245°, and is hydrolysed by boiling water with loss of  $1\text{CO}_2$ , yielding *ethyl sodiodicyanoglutaconate*,  $\text{CO}_2\text{Et}\cdot\text{CNa}(\text{CN})\cdot\text{CH}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$ , which crystallises in needles with  $2\text{H}_2\text{O}$ . *Ethyl dicyanoaconitate*,

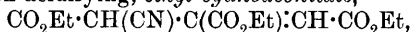


obtained by acidifying an aqueous solution of its sodium derivative, crystallises in leaflets, with  $\frac{1}{2}\text{H}_2\text{O}$ , melts and decomposes when rapidly heated at 145—146°, and cannot be recrystallised.

If, in the preceding decomposition by acid, the solution of the sodium derivative be very dilute, further hydrolysis occurs, and *ethyl*

*isoeiminodicarboxyaconitate*,  $\text{CO}_2\text{Et}\cdot\text{C}\begin{smallmatrix} \text{CH}(\text{CO}_2\text{Et})-\text{C}\cdot\text{NH} \\ \text{C}(\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{O} \end{smallmatrix}$ , is formed

(compare preceding abstract); it does not contain a carboxyl group since it is not acid in character, and crystallises from dilute alcohol in needles, with  $1\text{H}_2\text{O}$ , which melt at 70°. By warm dilute alkalis, it is dissolved, and, on acidifying, *ethyl cyanoaconitate*,



is precipitated as a heavy, yellowish oil with acid properties.

On boiling the isoimide with absolute alcohol, it undergoes isomeric change into *ethyl 5-carboxy-2:6-dihydroxycinchomeronate* (*ethyl 2:6-dihydroxypyridine-3:4:5-tricarboxylate*) or its isodynamic form, *ethyl 6-hydroxy-2-keto- $\Delta^{3,5}$ -dihydropyridinetricarboxylate*; the product crystallises from benzene on adding light petroleum in soft, white needles, melts at 137° and is converted by boiling hydrochloric acid of sp. gr. 1.06 into *ethyl 2:6-dihydroxy-3:4-cinchomeronate* (*ethyl 2:6-dihydroxy-3:4-pyridinedicarboxylate*), which crystallises from benzene or methyl alcohol in white leaflets and melts at 157°; citrazinic acid is also formed.

*Monoethyl 2:6-dihydroxycinchomeronate* (*ethyl 3-carboxy-2:6-dihydroxypyridine-4-carboxylate* or *ethyl 4-carboxy-2:6-dihydroxypyridine-3-carboxylate*), obtained by boiling ethyl 5-carboxy-2:6-dihydroxycinchomeronate with aqueous sodium hydroxide (2 mols.), crystallises from dilute alcohol in small needles and decomposes at 215°.

Ethyl tricyanotrimethylenetricarboxylate (*loc. cit.*) melts when pure at 119.5°; tricyanotrimethylene crystallises from alcohol in white leaflets and melts at 188—189°.

*Ethyl dicyanotrimethylenetetra-carboxylate*,  $\text{CO}_2\text{Et}\cdot\text{C}(\text{CN})\begin{smallmatrix} > \\ > \end{smallmatrix}\text{C}(\text{CO}_2\text{Et})_2$ ,

is always formed as one of the products of the interaction of ethyl bromocyanoacetate and sodiocyanoacetate; it crystallises best from

alcohol in large, transparent, triclinic crystals and is easily hydrolysed by barium hydroxide to trimethylenetetra-carboxylic acid (Schacherl, Abstr., 1885, 1125). W. A. D.

**Mixed Methenyl Compounds. IV. Synthesis of 2:5-Lutidine [2:5-Dimethylpyridine].** By GIORGIO ERRERA (*Ber.*, 1901, 34, 3691—3700).—*Ethyl ε-cyano-δ-ethoxy-β-hexanone-ε-carboxylamide-γ-carboxylate*,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CH}(\text{OEt})\cdot\text{CMe}(\text{CN})\cdot\text{CO}\cdot\text{NH}_2$ , obtained by the interaction of ethyl α-ethoxymethyleneacetate and methylecyanoacetamide (in the form of cyanoacetamide, methyl iodide, and sodium ethoxide in alcoholic solution), crystallises from water in flat, lustrous needles, and melts at  $202-203^\circ$ ; it is accompanied by considerable quantities of ethyl 5-cyano-6-hydroxy-2-methylpyridine-3-carboxylate, formed from unchanged cyanoacetamide (Abstr., 1900, i, 43), and of ethyl 6-hydroxy-2:5-dimethylpyridine-3-carboxylate (*infra*). *ε-Cyano-δ-ethoxy-β-hexanone-ε-carboxylamide-γ-carboxylic acid* obtained by hydrolysing the ethyl ester, separates from water in hard, opaque, white crystals, and melts and decomposes at  $256^\circ$ ; if the hydrolysis is effected by boiling hydrochloric acid, alcohol, ammonia, and carbon dioxide are eliminated and ring formation occurs with the production of *ethyl 6-hydroxy-2:5-dimethylpyridine-3-carboxylate*; this crystallises from alcohol in soft, colourless needles, melts at  $216-217^\circ$ , and is easily hydrolysed by boiling dilute alkalis into the corresponding acid, which crystallises from glacial acetic acid in slender needles and when rapidly heated melts and decomposes at  $300-305^\circ$ . *6-Hydroxy-2:5-dimethylpyridine*, obtained by heating the acid with hydrochloric acid of sp. gr. 1.1 for several hours at  $150^\circ$ , forms monoclinic crystals [ $a:b:c = 1.54256:1:1.43626$ ;  $\beta = 46^\circ 52' 57''$ ], with  $\frac{1}{2}\text{H}_2\text{O}$ , and melts at  $138-139^\circ$ ; the *potassium salt*,  $\text{C}_7\text{H}_8\text{ONK}\cdot\frac{5}{2}\text{H}_2\text{O}$ , crystallises in lustrous leaflets. *3-Bromo-6-hydroxy-2:5-dimethylpyridine*, formed by the action of bromine in glacial acetic acid solution, crystallises from alcohol in long, lustrous needles and melts at  $218-219^\circ$ . *2:5-Dimethylpyridine*, formed on distilling its hydroxy-derivative with zinc dust, boils at  $159-160^\circ$ , and yields a crystalline hydrochloride and two *mercurichlorides*,  $\text{C}_7\text{H}_{10}\text{NCl}\cdot 6\text{HgCl}_2$  (small, hard prisms) and  $2\text{C}_7\text{H}_{10}\text{NCl}\cdot 5\text{HgCl}_2$  (long, lustrous needles); the *picrate* melts at  $165.5^\circ$ . W. A. D.

**Action of Pyridine Bases on Tetrahalogen Derivatives of Quinones.** By HENRI IMBERT (*Compt. rend.*, 1901, 133, 937—938).—The compound obtained by the action of pyridine on tetrachloroquinone (this vol., ii, 55), when treated with hydrochloric acid and potassium chlorate, yields a *pyridyltrichlorotriketopentamethylene hydrochloride*,  $\text{HCl}\cdot\text{C}_5\text{NH}_4\cdot\text{CCl}\left\langle\begin{array}{c} \text{CO}\cdot\text{CCl}_2 \\ \text{CO}\cdot\text{CO} \end{array}\right.$ , forming white crystals somewhat soluble in cold water. With phenylhydrazine, it yields a trihydrazone, and with o-tolylenediamine it yields an azine. It follows that this oxidation product contains three ketonic groups, two of which are adjacent, and consequently the only admissible formula for the original product (*loc. cit.*) is  $\text{C}_5\text{NH}_4\cdot\text{C}_6\text{Cl}_2\text{O}_2\cdot\text{OH}$ . C. H. B.

**Tertiary and Quaternary Tetrahydroisoquinoline Bases; a Contribution to the Stereochemistry of Nitrogen.** By EDGAR WEDEKIND and E. OECHSLEN (*Ber.*, 1901, 34, 3986—3993. Compare Abstr., 1900, i, 155).—2-Methyltetrahydroisoquinoline can be readily prepared by reduction of isoquinoline methiodide by tin and hydrochloric acid (compare Ferratini, Abstr., 1893, i, 227). It is a colourless oil, distils at 212°, and has strongly basic properties. With ethyl iodacetate, it forms an *additive* product,  $C_{14}H_{20}O_2NI$ , which forms yellow crystals melting at 156—157°. 2-Ethyltetrahydroisoquinoline,  $C_9NH_9Et$ , obtained from isoquinoline ethiodide, is a pale yellow oil boiling at 225—227°; the *platinichloride* crystallises in reddish-yellow leaflets melting at 169°; the *picrate* in yellow needles melting at 121°; the normal *oxalate* in colourless needles melting at 110°; the *hydriodide* in pale yellow needles melting at 170°; the *additive* compound with ethyl iodacetate forms small crystals decomposing at 109—110°.

isoquinoline *benzylidide* crystallises in large, monoclinic plates [ $a:b:c=0.5842:1:1.3498$ ;  $\beta=82^\circ 16.5'$ ], and melts at 175—176°. On reduction, 2-benzyltetrahydroisoquinoline,  $C_{16}H_{17}N$ , is obtained as a pale yellow, viscous oil boiling at 194—197° under 18 mm. pressure; the *platinichloride* crystallises in brown pyramids decomposing at 219°; with ethyl iodacetate, an *additive* compound is obtained as crystals decomposing at 148—149°. Benzylethyltetrahydroisoquinolinium iodide is formed very readily from 2-ethyltetrahydroisoquinoline and benzyl iodide, far more slowly from 2-benzyltetrahydroisoquinoline and ethyl iodide; by both methods of preparation a salt is obtained crystallising in large plates which decompose at 133°. The crystals of both specimens are monoclinic, have  $\beta=63^\circ 40'$ , and are in all respects identical.

K. J. P. O.

**Condensation Products from Aromatic Nitroso-compounds and Methylene Derivatives.** By FRANZ SACHS (D.R.-P. 121974).—The compound produced by condensing benzyl cyanide and *p*-nitrosophenol in alcoholic sodium hydroxide solution, crystallises in brown needles, melts at 155°, and is converted by dilute mineral acids into the original cyanide and *p*-aminophenol. Corresponding condensation products are obtained from *p*-nitrosophenol and phenylmethylpyrazolone, ethyl acetoacetate, and cyanoacetamide.

G. T. M.

**Nitroso-*m*-phenylenediamine and Nitroso-2:4-tolylenediamine.** ERNST TAUBER and FRANZ WALDER (D.R.-P. 123375).—Nitroso-compounds are formed when cooled aqueous or slightly acid solutions of *m*-phenylenediamine and its tolyl homologue are rapidly treated with 2 mols. of nitrous acid. These substances are always accompanied by Bismarck-brown which is separated by the addition of sodium chloride, whilst the nitroso-derivatives are isolated by saturating the filtrate with ether and adding sodium carbonate.

Nitroso-*m*-phenylenediamine,  $NO \cdot C_6H_3(NH_2)_2$  (compare Abstr., 1901, i, 141), crystallises in red, monoclinic plates and melts at 210°; its hydrochloride separates from water in reddish-brown needles.

Nitroso-2:4-tolylenediamine,  $NO \cdot C_6H_2Me(NH_2)_2$ , closely resembles its lower homologue and melts at 195°.

G. T. M.



**Condensation Products from Aromatic *p*-Nitrosoamines and Toluene or Xylene Compounds.** By FRANZ SACHS (D.R.-P. 121745).—2:4-Dinitrobenzylidenedimethyl-*p*-phenylenediamine,  $C_6H_3(NO_2)_2 \cdot CH:N \cdot C_6H_4 \cdot NMe_2$ , produced by condensing 2:4-dinitrotoluene and nitrosodimethylaniline in boiling alcoholic solution in the presence of a small amount of sodium carbonate or trisodium phosphate, separates from glacial acetic acid as a brownish-violet, crystalline powder with a bronzy lustre; it melts at  $196^\circ$  and is sparingly soluble in the ordinary solvents.

2:4:6-Trinitrotoluene, 2:4:6-trinitro-*m*-xylene, and 2-chloro-4-nitrotoluene also yield similar condensation products obtained as dark brown powders. This reaction takes place only when the nitro-compound contains in its molecule at least one other negative radicle, negative results being obtained with *o*- and *p*-nitrotoluene. These condensation products on hydrolysis yield the corresponding benzaldehyde derivatives (compare Abstr., 1901, i, 230). G. T. M.

***m*-Aminotolylloxaminosulphonic Acids.** SCHOELLKOPF, HARTFORD & HANNA Co. (D.R.-P. 121746).—*m*-Aminotolylloxamino-5-sulphonic acid ("A" acid),  $NH_2 \cdot C_6H_2Me(NH \cdot CO \cdot CO_2H) \cdot SO_3H$ , obtained by heating 2:4-tolylenediamine-5-sulphonic acid with a 25 per cent. solution of oxalic acid, separates from the product of reaction in a crystalline form; it yields a sparingly soluble calcium salt, a stable diazo-compound which is precipitated even from dilute solutions, and a scarlet azo-derivative with R-salt.

The corresponding 2-aminotolyl-6-oxamino-4-sulphonic acid ("B" acid), produced from 2:6-tolylenediamine-4-sulphonic acid, yields a soluble calcium salt and diazo-compound, the azo-derivative with R-salt being orange. G. T. M.

**Condensation Products from the Diaminoanthraquinones and Formaldehyde.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 123745).—1:5-, 1:3-, and 1:8-Diaminoanthraquinones when heated with formaldehyde in methyl or ethyl alcohol, acetone, acetic acid, or carbon disulphide solution yield crystalline condensation products which are insoluble in water, acids, or alkalis, but dissolve in alcohol, giving red solutions. G. T. M.

**Naphthacridine Derivatives.** CARL ULLMANN (D.R.-P. 123260. Compare this vol., i, 55, 56).—Phenonaphthacridine,  $C_{10}H_6 \begin{smallmatrix} <N> \\ | \\ CH \end{smallmatrix} C_6H_4$ , (m. p.  $129.5^\circ$ ), is obtained by heating together trioxymethylene,  $\beta$ -naphthol, and aniline at  $160^\circ$ ; *o*-tolunaphthacridine, produced in a similar manner from *o*-toluidine, melts at  $143^\circ$ .

*Dimethylphenonaphthacridine*, prepared by heating the condensation product of formaldehyde and *m*-xylidine with  $\beta$ -naphthol, crystallises from alcohol or benzene in pale yellow needles and melts at  $152^\circ$ .

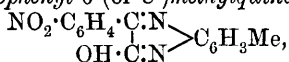
*Acetylmethylene-*p*-phenylenediamine*,  $NHAc \cdot C_6H_4 \cdot N:CH_2$ , obtained from acetyl-*p*-phenylenediamine and formaldehyde, forms white crystals melting at  $195$ — $200^\circ$ ; when treated with  $\beta$ -naphthol at  $150$ — $180^\circ$ ,

it yields *acetylaminophenonaphthacridine*,  $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{H} \end{smallmatrix} > C_6H_3 \cdot NHAc$ , a compound crystallising from alcohol in yellow needles and melting at  $255^\circ$ . The corresponding *aminophenonaphthacridine*, obtained by hydrolysing the acetyl derivative, crystallises in needles melting at  $238^\circ$ .  
G. T. M.

**1-Phenyl-2:3-dimethyl-5-thiopyrazolone.** AUGUST MICHAELIS (D.R.-P. 122287).—1-Phenyl-2:3-dimethyl-5-thiopyrazolone,  $C_{11}H_{12}N_2S$ , obtained by treating the metho-chloride, -bromide, or -iodide of 5-chloro-1-phenyl-3-methylpyrazole,  $C_{11}H_{12}N_2Cl_2$ , with an alkali sulphide or hydrosulphide, separates from water or alcohol-ether in white crystals and melts at  $166^\circ$ ; it forms a crystalline hydrochloride (compare Abstr., 1901, i, 52).  
G. T. M.

**Isatin.** By J. BURACZEWSKI and LEON MARCHLEWSKI (*Ber.*, 1901, 34, 4008—4015. Compare Abstr., 1901, i, 415, 615).—*o*-Nitrobenzoylformic acid condenses with *o*-phenylenediamine hydrochloride in the presence of sodium acetate, forming 2-hydroxy-3-*o*-nitrophenylquinoxaline,  $NO_2 \cdot C_6H_4 \cdot \begin{smallmatrix} \text{C}:\text{N} \\ | \\ \text{OH} \cdot \text{C}:\text{N} \end{smallmatrix} > C_6H_4$ , which crystallises in yellowish needles melting at  $295^\circ$  and is soluble in alkalis; its alkaline solution is reduced by ferrous sulphate with the formation of 2-hydroxy-3-*o*-aminophenylquinoxaline; the constitution of the latter compound, which is also obtained from acetylisatin and *o*-phenylenediamine, is therefore confirmed (*loc. cit.*).

2-Hydroxy-3-*o*-nitrophenyl-6-(or 8-)methylquinoxaline,



prepared from *o*-tolylenediamine and *o*-nitrobenzoylformic acid, crystallises in yellowish needles melting at  $293$ — $294^\circ$ . 2-Hydroxy-6-(or 8-)

ethoxy-3-*o*-nitrophenylquinoxaline,  $NO_2 \cdot C_6H_4 \cdot \begin{smallmatrix} \text{C}:\text{N} \\ | \\ \text{OH} \cdot \text{C}:\text{N} \end{smallmatrix} > C_6H_3 \cdot OEt$ , prepared

from ethoxy-*o*-phenylenediamine [ $NH_2:NH_2:OEt = 1:2:4$ ] and *o*-nitrobenzoylformic acid, is a yellowish solid melting at  $215$ — $216^\circ$ . 2-Hydroxy-3-phenylquinoxaline, prepared in an analogous manner, crystallises in pale yellow needles melting at  $247^\circ$ ; 2-Hydroxy-6-(or 8-)ethoxy-3-phenylquinoxaline, crystallises in yellow needles melting at  $205^\circ$ . 2-Hydroxy-3-*o*-aminophenyl-6-(or 8-)methylquinoxaline, which crystallises in dark yellow needles melting at  $208$ — $209^\circ$ , is formed as an acetyl derivative from acetylisatin and *o*-tolylenediamine together with acetylmethylindophenazine; it is separated from the latter by treatment with alkalis, in which the quinoxaline alone dissolves; the acetyl group is eliminated by prolonged boiling of the alkaline solution.

Methyl- $\psi$ -isatin and *o*-phenylenediamine condense when heated in acetic acid solution, forming 11-methylindophenazine,  $C_6H_4 \cdot \begin{smallmatrix} \text{C}:\text{N} \\ | \\ NMe \cdot \text{C}:\text{N} \end{smallmatrix} > C_6H_4$ , (Abstr., 1896, i, 236), which forms yellow crystals melting at  $148^\circ$ , and with concentrated hydrochloric acid gives an orange hydrochloride. This substance is also formed when indophenazine is methylated.

11-*Benzylindophenazine* is obtained from indophenazine and benzyl chloride, and crystallises in orange-yellow needles melting at  $171.5^{\circ}$ ; it is also produced by the condensation of benzyl- $\psi$ -isatin and *o*-phenylenediamine.

With 4-ethoxy-*o*-phenylenediamine, isatin yields a mixture of two ethoxyindophenazines (see Abstr., 1899, i, 719). These can be separated by conversion into the acetyl derivatives and recrystallisation of the latter from alcohol.  $\alpha$ -d-*Ethoxyindophenazine* is obtained from the more sparingly soluble acetyl derivative (m. p.  $208^{\circ}$ ) and crystallises in yellow needles melting at  $265^{\circ}$ ;  $\beta$ -d-*ethoxyindophenazine*, obtained from the soluble acetyl derivative (m. p.  $165^{\circ}$ ), is a yellow substance melting at  $230^{\circ}$ .

Isatin and 3:4-diaminobenzoic acid condense to an *indophenazine-7-(or 8)-carboxylic acid*, which is obtained as a crystalline powder melting above  $300^{\circ}$ ; 10-*methyl- $\psi$ -indophenazine*,  $\begin{matrix} \text{C}_6\text{H}_4 \cdot \text{C} \equiv \text{N} \\ \text{N} = \text{C} \cdot \text{NMe} \end{matrix} > \text{C}_6\text{H}_4$ ,

is prepared from isatin and *o*-aminomethylaniline and crystallises in red needles melting at  $175$ – $176^{\circ}$ ; the *hydrochloride* forms a yellow, crystalline powder. 10-*Phenyl- $\psi$ -indophenazine*, prepared from isatin and *o*-aminodiphenylamine, crystallises in lustrous needles melting at  $265$ – $266^{\circ}$ . Treatment of these two derivatives of  $\psi$ -indophenazine with concentrated acids leads to the formation of indophenazine and not of  $\psi$ -indophenazine.

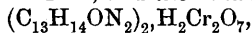
K. J. P. O.

*p*-Tolylpyridazine and its Derivatives. By A. KATZENELLENBOGEN (*Ber.*, 1901, 34, 3828–3839. Compare Gabriel and Colman, Abstr., 1899, i, 390).—A 71 per cent. yield of  $\beta$ -*p*-toluoylpropionic acid (Abstr., 1888, 951) is obtained when succinic anhydride, toluene, and aluminum chloride are shaken for fifteen hours at the ordinary temperature. When warmed with hydrazine sulphate and sodium hydroxide, the acid is transformed into 3-*p*-tolylpyridazinone,  $\text{C}_7\text{H}_7 \cdot \text{C} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{N} - \text{NH} \end{smallmatrix} > \text{CO}$ , which crystallises from alcohol in prisms melting at  $155$ – $156^{\circ}$ . An acetic acid solution of bromine converts the pyridazinone into 3-*p*-tolylpyridazone,  $\text{C}_7\text{H}_7 \cdot \text{C} \begin{smallmatrix} \text{CH} : \text{CH} \\ \text{N} - \text{NH} \end{smallmatrix} > \text{CO}$ , which crystallises from acetic acid in hexagonal plates melting at  $225^{\circ}$ , and is soluble in dilute alkalis, but only sparingly so in ether, alcohol, or benzene. When methylated, it yields 3-*p*-tolyl-1-methylpyridazone,  $\text{C}_7\text{H}_7 \cdot \text{C} \begin{smallmatrix} \text{CH} : \text{CH} \\ \text{N} \cdot \text{NMe} \end{smallmatrix} > \text{CO}$ , crystallising in colourless needles and melting at  $125^{\circ}$ . The corresponding *ethyl* derivative melts at  $96$ – $97^{\circ}$ .

6-*Chloro-3-p*-tolylpyridazine,  $\text{C}_7\text{H}_7 \cdot \text{C} \begin{smallmatrix} \text{CH} : \text{CH} \\ \text{N} - \text{N} \end{smallmatrix} > \text{CCl}$ , obtained by the action of phosphorus oxychloride on the pyridazone, crystallises in pointed prisms, melts at  $153^{\circ}$ , and is readily soluble in most organic solvents.

6-*Methoxy-3-p*-tolylpyridazine crystallises in four-sided plates melting at  $114$ – $115^{\circ}$ ; its *platinichloride* forms golden-yellow crystals melting at  $177$ – $179^{\circ}$ . The *ethoxy*-derivative crystallises in needles melting at  $106^{\circ}$ , its *picrate* forms lemon-yellow needles melting at  $118^{\circ}$ , the

*platinichloride* melts and decomposes at  $146^{\circ}$ , the *aurichloride* softens at  $130^{\circ}$  and melts at  $150$ — $151^{\circ}$ , and the *dichromate*,



is an orange-red powder softening at  $65^{\circ}$  and melting at about  $106^{\circ}$ . 6-Phenoxy-3-*p*-tolylpyridazine forms slender, colourless needles melting at  $135^{\circ}$ .

6-Iodo-3-*p*-tolylpyridazine forms, minute crystals melting at  $188^{\circ}$ , and when reduced with hydriodic acid and phosphorus yields 3-*p*-tolylpyridazine, which crystallises in glistening, four-sided plates melting at  $106$ — $107^{\circ}$  and is readily soluble in most organic solvents; the *picrate* crystallises in prisms melting at  $151^{\circ}$ , the *platinichloride* decomposes at about  $125^{\circ}$ , and the *aurichloride* softens at  $147^{\circ}$  and melts at about  $198^{\circ}$ .

Nitro-3-*p*-tolylpyridazine,  $\text{NO}_2 \cdot \text{C}_7\text{H}_6 \cdot \text{C}_4\text{N}_2\text{H}_3$ , crystallises in colourless needles melting at  $133^{\circ}$ ; the *picrate* sinters at  $170^{\circ}$  and melts at about  $184^{\circ}$ ; the *platinichloride* melts and decomposes at  $258^{\circ}$ , and the *aurichloride* melts at  $211$ — $212^{\circ}$ .

Amino-3-*p*-tolylpyridazine, obtained by reducing the nitro-compound with stannous chloride, crystallises from water in needles melting at  $142$ — $143^{\circ}$ , the *picrate* melts and decomposes at  $170$ — $171^{\circ}$ , the *platinichloride* does not melt at  $260^{\circ}$ , and the *benzoyl* derivative melts at  $178$ — $179^{\circ}$ .

Hydroxy-3-*p*-tolylpyridazine crystallises from alcohol in prisms, and melts at  $210$ — $211^{\circ}$ ; its *hydrochloride* forms colourless needles, the *dichromate*, orange-yellow crystals, and the *platinichloride* pointed prisms melting and decomposing at  $175^{\circ}$ .

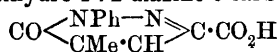
On oxidation with alkaline permanganate, *p*-tolylpyridazine yields pyridazyl-3-*p*-benzoic acid,  $\text{C}_4\text{N}_2\text{H}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , in the form of needles, sparingly soluble in the usual solvents and infusible at  $270^{\circ}$ .

*p*-Tolylpyridazine and methyl iodide unite to form a *methiodide*,  $\text{C}_{12}\text{H}_{13}\text{N}_2\text{I}$ , which turns red at  $94^{\circ}$  and melts at  $182$ — $183^{\circ}$ .

The *picrate* of the methyl base,  $\text{C}_{11}\text{H}_{10}\text{N}_2\text{Me} \cdot \text{C}_6\text{H}_2\text{O}_7\text{N}_3$ , forms lemon-yellow prisms sintering at  $174^{\circ}$  and melting at  $183$ — $184^{\circ}$ , and the *platinichloride*,  $(\text{C}_{11}\text{H}_{10}\text{N}_2\text{Me})_2\text{PtCl}_6$ , melts and decomposes at  $214$ — $215^{\circ}$ .

*p*-Tolylpyrrolidine,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{CH} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{NH} \cdot \text{CH}_2 \end{smallmatrix}$ , obtained by reducing *p*-tolylpyridazine with sodium and alcohol, is an oil and is volatile with steam; the *picrate* sinters at  $145^{\circ}$  and melts at  $150^{\circ}$ ; no other salts were obtained in a crystalline state. A further product formed on reduction is 3-*p*-tolylhexahydropyridazine; its *nitrate* forms colourless prisms melting at  $186^{\circ}$  and the *picrate* melts and decomposes at  $167$ — $168^{\circ}$ .  
J. J. S.

Action of Hydrochloric Acid on Pyruvic Acid. By A. W. K. DE JONG (*Annalen*, 1901, 319, 121—128. Compare Abstr., 1899, i, 483; 1901, i, 446).—The phenylhydrazone of the  $\alpha$ -lactone of  $\alpha$ -keto- $\gamma$ -hydroxybutane- $\alpha$ -dicarboxylic acid, when heated with hydrochloric acid of sp. gr. 1.14 yields 3-keto-2-phenyl-4-methyl-2:3-dihydro-1:2-diazine-6-carboxylic acid,

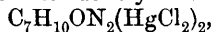


(compare Ruhemann, Abstr., 1894, i, 425). The employment of stronger acid of sp. gr. 1.20 in this experiment leads to the production of the *compound*,  $C_{12}H_{10}O_3N_2$ , crystallising from glacial acetic acid in white needles and melting at  $280^\circ$ . This substance is insoluble in a solution of alkali carbonate, but dissolves in one of sodium hydroxide; the addition of hydrochloric acid to the alkaline solution causes the precipitation of the monobasic *acid*,  $C_{12}H_9O_4N \cdot H_2O$ , a compound separating in yellow needles or plates and melting at  $237-238^\circ$ . The new acid forms a readily soluble *potassium* salt and the compound, when boiled with strong hydrochloric acid, regenerates the anhydrous acid,  $C_{12}H_9O_4N$ , which has the same melting point as its hydrate. Both forms of the acid, when treated with hydrochloric acid of sp. gr. 1.14, yield a compound, crystallising in white needles, which is readily decomposed by water. G. T. M.

**4:6-Dimethylpyrimidine.** By ST. ANGERSTEIN (*Ber.*, 1901, 34, 3956—3963. Compare Gabriel and Colman, Abstr., 1899, i, 638).—

*2-Chloro-4:6-dimethylpyrimidine*,  $CCl \begin{smallmatrix} \diagup N \cdot CMe \\ \diagdown N \cdot CMe \end{smallmatrix} CH$ , obtained by the action of phosphorus oxychloride on oxydimethylpyrimidine (Abstr., 1894, i, 111), melts at  $38^\circ$ , distils at  $223.3^\circ$  under 756 mm. pressure, dissolves readily in water, alcohol, or ether, and gives a crystalline compound with mercuric chloride. When reduced with zinc dust and water, it yields 4:6-dimethylpyrimidine (Gabriel and Colman, *loc. cit.*), which, on oxidation with permanganate, yields *pyrimidine-4:6-dicarboxylic acid*, crystallising in needles and decomposing at  $222^\circ$ . The acid yields a colourless *hydrochloride*, a yellow *platinichloride*, and a pale green *copper* salt,  $C_6H_2O_4N_2Cu$ . When less permanganate is employed, *4-methylpyrimidine-6-carboxylic acid*,  $CH \begin{smallmatrix} \diagup N = CMe \\ \diagdown N \cdot C(CO_2H) \end{smallmatrix} CH$ , is obtained; it crystallises in needles, melts and decomposes at  $165-166^\circ$ , and is readily soluble in water. The *copper* and *silver* salts have been prepared.

Chlorodimethylpyrimidine readily reacts with an alcoholic solution of sodium methoxide, yielding *2-methoxy-4:6-dimethylpyrimidine*, which crystallises in prisms, melts at  $35-36^\circ$ , and distils at  $208-209^\circ$  under 744 mm. pressure. It combines with hydrochloric acid, whilst with mercuric chloride it yields a *compound*,



which crystallises in needles soluble in hot water or alcohol. *2-Ethoxy-4:6-dimethylpyrimidine* is a colourless, strongly refractive oil boiling at  $220.1^\circ$  under 764 mm. pressure; it is appreciably soluble in water, and yields a *compound*,  $C_9H_{12}ON_2 \cdot HgCl_2$ , sparingly soluble in water. The *hydrochloride* is readily soluble and precipitates are not obtained with auric chloride, platinic chloride, potassium dichromate, or sodium picrate. On treatment with bromine water, *5-bromo-2-ethoxy-4:6-dimethylpyrimidine*, melting at  $40-41^\circ$  and boiling at  $254^\circ$  is obtained.

*2-Phenoxy-4:6-dimethylpyrimidine* melts at  $81^\circ$ , distils at  $305-312^\circ$ , and is very sparingly soluble in water. With mercuric chloride, it yields the *compound*  $C_{12}H_{12}ON_2 \cdot 2HgCl_2$ , crystallising in needles and

soluble in alcohol or hot water; the *hydrochloride* is readily soluble in both water and alcohol. 2-Anilino-4:6-dimethylpyrimidine crystallises from toluene in hexagonal plates melting at 88—89° and is insoluble in water; the *platinichloride*,  $(C_{12}H_{13}N_3)_2 \cdot H_2PtCl_6$ , crystallises in yellow needles and the *picrate* in yellow plates melting at 186°. It yields a *nitroso-derivative*,  $C_4N_2HMe_2 \cdot NPh \cdot NO$ , which crystallises in well-developed prisms melting at 130—131°; the *picrate* melts at 184° and the *platinichloride* crystallises in yellow needles.

2-Amino-4:6-dimethylpyrimidine, obtained by heating the chlorobase with alcoholic ammonia at 100°, crystallises in needles melting at 150—152°. The *platinichloride* forms yellow prisms melting at 225°. The *hydrochloride* melts at 181° and is readily soluble in alcohol or water. The *picrate* crystallises in yellow plates and melts at 230°, and the compound with mercuric chloride,  $C_6H_9N_3 \cdot HgCl_2$ , crystallises in colourless needles.

4:6-Dimethylpyrimidyl 2-mercaptan,  $C_4N_2HMe_2 \cdot SH$ , crystallises in yellow, glistening needles melting at 198° and on oxidation yields 4:6-dimethylpyrimidine 2-disulphide,  $S_2(C_4N_2HMe_2)_2$ , melting at 162—163° and soluble in acids and in most organic solvents.

J. J. S.

**Synthesis of Uracil, Thymine, and Phenyluracil.** By EMIL FISCHER and GEORG ROEDER (*Ber.*, 1901, 34, 3751—3763. Compare *Abstr.*, 1901, i, 294).—*Bromohydrouracil* separates from water or alcohol as a colourless, granular powder; it dissolves in about 5 parts of boiling water or 10 parts of boiling alcohol, but is insoluble in ether or carbon disulphide.

*Hydroxyhydrouracil*,  $C_4H_6O_3N_2$ , a substance the constitution of which was not determined, but differs from that of uracil in containing an additional  $H_2O$ , is the chief product of the action of alkalis on bromohydrouracil; it dissolves in 12 times its weight of water, crystallises on cooling in colourless, flat needles, and melts at 228° (corr.) with partial decomposition when quickly heated. By heating bromohydrouracil with pyridine, uracil itself ( $C_4H_4O_2N_2$ ) is formed; it crystallises from hot water in minute, colourless needles, and when quickly heated becomes brown at about 280° and melts with liberation of gas at 335°.

4-Phenylhydrouracil,  $CO \begin{smallmatrix} \text{NH} \text{---} \text{CO} \\ \text{NH} \cdot \text{CHPh} \end{smallmatrix} CH_2$ , prepared from carbamide and cinnamic acid, crystallises from alcohol in prismatic needles, melts at 202—203° (corr.), and dissolves in about 25 parts of hot water or 20 parts of boiling alcohol; it dissolves readily in cold dilute alkalis or in concentrated hydrochloric acid.

4-Phenylbromouracil,  $C_{10}H_9O_2N_2Br$ , crystallises in minute, pointed needles and melts at about 214° (corr.) with liberation of hydrogen bromide. 4-Phenyluracil,  $C_{10}H_8O_2N_2$ , crystallises in microscopic needles and melts and decomposes at 267° (corr.).

T. M. L.

**Condensation Products of 1:8-Naphthylenediamine and its Derivatives with Acetone.** BADISCHE ANILIN- & SODA-FABRIK (D. R.-P. 122475).—1:8-Naphthylenediamine sulphate, or the sodium

salt of one of its sulphonic acids, readily condenses with acetone in slightly acid solution. The *condensation product* from the diamine itself has the formula  $C_{10}H_6 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} > CMe_2$ ; the substance  $C_{13}H_{14}O_3N_2S$ , has also been prepared from 1 : 8-naphthylenediamine-4-sulphonic acid. 1 : 8-Naphthylenediamine-2 : 3-disulphonic acid and 4-chloro-1 : 8-naphthylenediamine give rise to similar derivatives. G. T. M.

**Homologues of Xanthine.** C. F. BOEHRINGER & SÖHNE (D.R.-P. 121224).—8-Methylxanthine,\*  $CMe \begin{smallmatrix} \text{NH} \cdot \text{C} \cdot \text{CO} \cdot \text{NH} \\ \diagup \quad \diagdown \\ \text{N} - \text{C} \cdot \text{NH} \cdot \text{CO} \end{smallmatrix}$ , is produced by heating uric acid with acetic anhydride (10 parts) until the insoluble residue no longer reduces ammoniacal silver nitrate; the crude base, purified by conversion into its potassium derivative and reprecipitation with dilute acid, crystallises in colourless prisms or plates which are very sparingly soluble in water and melt above  $400^\circ$ . The *hydrochloride* separates from a concentrated hydrochloric acid solution in colourless, lustrous prisms. The methylxanthine readily dissolves in solutions of ammonia or the alkali hydroxides and yields a stable, gelatinous silver derivative with ammoniacal, and a flocculent double salt with neutral, silver nitrate. The condensation is accelerated either by adding a tertiary base (pyridine, quinoline, or dimethylaniline) or by conducting the operation under pressure at  $180-185^\circ$ .

8-Ethylxanthine results when propionic anhydride is employed; this base resembles its lower homologue, but is more soluble in water; it darkens at  $350^\circ$  and decomposes at  $390^\circ$ . 8-isoPropylxanthine, prepared in a similar manner from isobutyric anhydride, crystallises in short prisms, darkens at  $340^\circ$ , and decomposes at  $380^\circ$ ; it is twice as soluble in water as the ethyl compound, but otherwise resembles the latter in dissolving in dilute acids or in solutions of ammonia or the alkali hydroxides, and in yielding a stable silver derivative with ammoniacal silver nitrate.

3 : 8-Dimethylxanthine,  $CMe \begin{smallmatrix} \text{NH} \cdot \text{C} - \text{CO} - \text{NH} \\ \diagup \quad \diagdown \\ \text{N} - \text{C} \cdot \text{NMe} \cdot \text{CO} \end{smallmatrix}$ , obtained by condensing 3-methyluric acid (Abstr., 1900, i, 63) with acetic anhydride in the presence of pyridine, crystallises from water in colourless, felted needles containing  $1H_2O$ ; it darkens at  $320^\circ$  and decomposes at  $350^\circ$ .

1 : 3 : 8-Trimethylxanthine,  $CMe \begin{smallmatrix} \text{NH} \cdot \text{C} - \text{CO} - \text{NMe} \\ \diagup \quad \diagdown \\ \text{N} - \text{C} \cdot \text{NMe} \cdot \text{CO} \end{smallmatrix}$ , derived from 1 : 3-dimethyluric acid, crystallises in needles or prisms, melts at  $325^\circ$ , and is the most soluble of these xanthine derivatives, dissolving in 40 parts of water; with silver nitrate and nitric acid, it yields a crystalline, double salt, and with an ammoniacal solution of the same reagent a gelatinous, silver derivative. G. T. M.

**New Synthesis of Fluorindine.** By RUDOLF NIETZKI and JOSEF SLABOSZEWICZ (Ber., 1901, 34, 3727—3732).—5'-Chloro-2' : 4'-dinitro-2-aminodiphenylamine,  $NH_2 \cdot C_6H_4 \cdot NH \cdot C_6H_2Cl(NO_2)_2$ , prepared from

\* The positions are numbered in accordance with the scheme proposed by E. Fischer (Ber., 1897, 30, 557; compare Abstr., 1897, i, 268, line 4, where positions 8 and 9 should be interchanged).

*o*-phenylenediamine and dichlorodinitrobenzene, forms orange-yellow crystals and melts at 232°; *o*-diaminodiphenyl-4:6-dinitro-1:3-phenylenediamine,  $C_6H_2(NO_2)_2(NH \cdot C_6H_4 \cdot NH_2)_2$ , crystallises from xylene in glistening, yellow flakes and melts at 253°. Diaminodiphenyltetraminobenzene,  $C_6H_2(NH_2)_2(NH \cdot C_6H_4 \cdot NH_2)_2$ , forms a hydrochloride and a crystalline double salt with zinc chloride. Aminophenyldiaminophenazine,  $C_6H_4 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} C_6H_2(NH) \cdot NH \cdot C_6H_4 \cdot NH_2$ , is a brown, crystalline powder and forms a hydrochloride.

Phenofluorindine (homofluorindine),  $C_6H_4 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} C_6H_2 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} C_6H_4$ , is formed on boiling the preceding compound with dilute hydrogen chloride, and is identical with the substance prepared by Caro.

Dimethylfluorindine (tolufluorindine), prepared from *o*-tolylenediamine,  $[(NH_2)_2 \cdot Me = 3:4:1]$ , was prepared by a similar method, and is perhaps identical with the compound prepared by Föhrenbach (*Diss., Basel*, 1898).  
T. M. L.

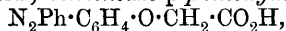
**Derivatives of the Phenyl Ethers.** By CARL HAEUSSERMANN and OSCAR SCHMIDT (*Ber.* 1901, 34, 3769—3771).—*o*-Azoxyphenyl ether, obtained by reducing *o*-nitrophenyl ether dissolved in alcohol containing sodium acetate in the cathode cell with an electric current of 2 amperes and 6 volts, crystallises in yellowish-red leaflets and melts at 95°. *p*-Azoxyphenyl ether, produced in a similar manner from *p*-nitrophenyl ether, crystallises in orange-yellow needles and melts at 115°. *p*-Azoxyphenyl *p*-tolyl ether from *p*-nitrophenyl tolyl ether (m. p. 69°) crystallises in lustrous-yellow leaflets and melts at 142°. Quinol *p*-azoxydiphenyl ether, from quinol *p*-nitrodiphenyl ether, obtained by the action of a current of 2 amperes and 25 volts on a dilute alcoholic solution of the nitro-derivative, crystallises, in light yellow leaflets and melts at 183°.

The corresponding amino-derivatives are obtained by the use of a tin cathode (compare Boehringer & Sons, *Abstr.*, 1901, i, 684).

*p*-Aminophenyl *p*-tolyl ether, produced in this way, crystallises from water in white needles and melts at 123°.

*p*-Azophenyl *p*-tolyl ether is prepared by reducing *p*-nitrophenyl *p*-tolyl ether with zinc dust and alcoholic potassium hydroxide and oxidising the resulting hydrazo-derivative with atmospheric oxygen; it forms small leaflets melting at 175°. Quinol *p*-azodiphenyl ether crystallises from benzene in lustrous, yellowish-red leaflets melting at 210°.  
G. T. M.

**Action of Monochloroacetic Acid on *p*-Hydroxyazobenzene.** By JUL. MAI and FRITZ SCHWABACHER (*Ber.*, 1901, 34, 3936—3941).—Neither diazobenzene chloride nor *p*-diazobenzenesulphonic acid react with phenoxyacetic acid; benzeneazo-*p*-phenoxyacetic acid,

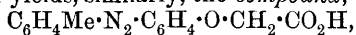


is, however, obtained by the action of sodium chloroacetate on the sodium derivative of *p*-hydroxyazobenzene; it crystallises from water in long, yellow needles, melts at 193°, and forms a sodium salt insoluble in alcohol and an ethyl ester, which is a green, crystalline compound



melting at 70°. The corresponding *p*-sulphonic acid was obtained by the action of sodium chloroacetate on phenolazo-*p*-benzenesulphonic acid and forms slightly soluble *potassium sodium*, *potassium hydrogen*, and *barium* salts. The *p*-nitro-derivative, obtained from *p*-nitrobenzenazophenol, crystallises in lustrous red needles, melts at 205°, and forms a crystalline, violet-coloured *sodium* salt. The phenoxy-acid, when reduced with stannous chloride, yields a *compound* which melts at 225°, forms a soluble *barium* salt, and is probably the semidine,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ ; the *sodium* salt, when similarly reduced, yields a *compound* which crystallises in colourless needles, melts at 239°, forms a slightly soluble, crystalline *barium* salt, and is probably the hydrazo-compound,  $\text{NHPh} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ .

*p*-Cresolazobenzene, when treated with chloroacetic acid, yields the *compound*,  $\text{N}_2\text{Ph} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , which melts at 123°; *p*-tolueneazophenol yields, similarly, the *compound*,



which melts at 200°; the dibasic *acid* from *p*-aminobenzoic acid melts at 285° and forms an easily soluble *sodium* salt; the *acid* obtained by treating diphenyltetrazophenol with chloroacetic acid crystallises in brown needles and melts at 255°.

R. H. P.

**Diphenyl Derivatives.** By ERNST BÖRNSTEIN (*Ber.*, 1901, 34, 3968—3969. Compare Ullmann and Forgan, this vol., i, 89).—When aniline (1 mol.) is diazotised in hydrochloric acid solution and then mixed with a colourless solution of copper sulphate (1 mol.) in sodium thiosulphate (6 mols.), in other words, with cuprous sodium thiosulphate, it yields phenyl sulphide and benzenediazodiphenyl (Griess, *Ber.*, 1876, 9, 132). *o*- and *p*-Toluidine and sulphanilic acid yield sulphides but not diphenyl derivatives on similar treatment;  $\alpha$ -naphthylamine yields  $\alpha$ -azonaphthalene.

J. J. S.

**Reduction, in an Alkaline Solution, of 2:4:5-Trimethylbenzalazine and the Preparation of some Derivatives of the Reduction Products.** By EVERHART P. HARDING (*J. Amer. Chem. Soc.*, 1901, 23, 829—842).—A more detailed account of work previously published (*Abstr.*, 1900, i, 613—614).

E. G.

**Conversion of *o*-Aziminobenzaldehyde into Anthranil.** By EUGEN BAMBERGER and ED. DEMUTH (*Ber.*, 1901, 34, 3874—3877).—When heated with water at 110° for 2 hours, or alone at 120°, *o*-aziminobenzaldehyde,  $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_3$ , is converted into anthranil, for which the constitution  $\text{C}_6\text{H}_4 \cdot \text{N} \begin{smallmatrix} \diagup \\ \text{CH} \end{smallmatrix} \text{O}$  is suggested; the anthranilic acid formed by the action of alkalis (*Abstr.*, 1901, i, 391), represents a product of further change. Similarly, 3:5-dichloro-6-aziminobenzaldehyde and 4:6-dimethyl-1-azimino-2-benzaldehyde are converted respectively into dichloroanthranil and dimethylantranil by heating with water. The melting point of dichloroanthranil is 112.5—113.2° (corr.) and not 96—97° (Friedländer and Schreiber, *Abstr.*, 1895, i, 524).

T. M. L.

**The Present Condition of the Chemistry of Albumin.** By ALBRECHT KOSSEL (*Ber.*, 1901, 34, 3214—3245).—A review of the recent advances in the chemistry of albumin, with an extensive bibliography of the subject. G. T. M.

**The Present Condition of the Chemistry of Albumin.** By ERNST SALKOWSKI (*Ber.*, 1901, 34, 3884—3885).—A question of priority in relation to Kossel's lecture (preceding abstract).

K. J. P. O.

**Decomposition of Albumin.** By MAXIMILIANO DENNSTEDT (*Chem. Zeit.*, 1901, 25, 832—836. Compare Abstr., 1901, i, 780).—It is thought probable that albumoses and peptones are formed simultaneously during the decomposition of proteids. Chittenden's name, *proteoses*, for all proteid-like decomposition products of proteids is suggested as a general term in place of 'albumose and peptone, whilst, when the source of the proteose is known, special names, for example, caseinose, fibrinose, albumose, &c., are used. The method of formation can also be indicated by prefixes such as pepto-, trypto-, bacteri-, acid-, alkali-, &c. When wheat fibrin or zein is boiled with baryta water, part of the nitrogen of the proteid is evolved as ammonia and part of the sulphur converted into barium sulphide or sulphate. From wheat fibrin, five distinct proteoses have been isolated and analysed. They all have strong acidic properties and may be titrated by the aid of standard alkali; the results vary, however, with the indicator employed, and they are all probably polybasic acids. Two definite products have been obtained from zein, and these also have acid properties. When zein is heated with water at pressures below 0.22 atmosphere, it is transformed into an insoluble modification having the same composition. As the pressure is increased, ammonia and hydrogen sulphide are formed, together with proteoses which have acidic properties and are present as ammonium salts in the final product. Three of these proteoses have been obtained and analysed; they appear to be more nearly allied to zein than the proteoses obtained by the aid of baryta water, and all give the Millon and biuret reactions.

It is thought that the formation of proteoses from proteids is not merely a hydrolytic action, but is a complex chemical decomposition accompanied by loss of nitrogen and sulphur; water is taken up, and oxidation probably occurs. J. J. S.

**Nature of Enzymes.** By THOMAS BOKORNY (*Chem. Centr.*, 1901, ii, 1210; from *Pharm. Centralhalle*, 42, 681—684).—The similarity of the behaviour of the enzymes to that of protoplasm indicates that the former substances are active albumins (protoplasmprotein) belonging to the group of nuclealbumins. The original paper contains a table in which descriptions of the properties of these substances are placed side by side. The enzymes are contained in, and secreted by, the living protoplast, and can be regenerated in the necessary quantity. E. W. W.

## Organic Chemistry.

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**Law governing the Formation of Additive Products and their subsequent Decomposition.** By ARTHUR MICHAEL [with T. H. MIGHILL] (*Ber.*, 1901, 34, 4215—4226).—Comparative experiments on the elimination of bromine by means of zinc from the bromides of various unsaturated compounds show the general applicability of the law that, in a series of isomeric or homologous additive products, those which are formed the most readily are also those which are most readily decomposed. In the case of the dibromides of the series ethylene to *isobutylene*, the amount of bromine which zinc eliminates increases as the series is ascended. Experiments with the isomeric ethyl dibromosuccinates, ethyl dibromomethylsuccinates, and methyl  $\alpha\beta$ -dibromocrotonates are also described. Of the two isomeric  $\beta$ -bromocinnamic acids, the one with the higher melting point is the more readily converted into phenylpropionic acid.

The *methyl* ester of the  $\alpha\beta$ -dibromocrotonic acid, which melts at  $94^\circ$ , is a colourless liquid which boils at  $94^\circ$  under 11 mm. pressure; the *methyl* ester of the isomeric acid (m. p.  $120^\circ$ ) is a colourless liquid which boils at  $102$ — $104^\circ$  under 14 mm. pressure.

R. H. P.

**Fluorobromo-derivatives containing Two Atoms of Carbon.** IV. By FRÉDÉRIC SWARTS (*Bull. Acad. Roy. Belg.*, 1901, 7, 383—414. Compare Abstr., 1898, i, 457; 1899, i, 254).—*Diffuorobromoethane*,  $\text{CHF}_2\cdot\text{CH}_2\text{Br}$ , obtained in theoretical quantity by heating together, at  $100^\circ$ , 2 mols. of antimony trifluoride and 3 mols. of tribromoethane, is a colourless, very volatile liquid with an agreeable ethereal odour; it has a sp. gr.  $1\cdot82443$  at  $18\cdot5^\circ$ , and  $1\cdot83685$  at  $10\cdot5^\circ$ ;  $n_D$   $1\cdot39300$ ,  $n_D$   $1\cdot39400$ , and  $n_H$   $1\cdot4047$  at  $10\cdot5^\circ$ . It is only slightly soluble in water, and mixes in all proportions with organic solvents. When cooled in liquid air, it solidifies to a crystalline mass which melts at  $-74\cdot5^\circ$ . It is not acted on by oxidising agents. When heated at  $180^\circ$  with bromine and ferric bromide, it yields tetrabromoethane, and when reduced with zinc in sodium hydroxide solution yields fluoroethylene. *Fluoroethylene*,  $\text{C}_2\text{H}_3\text{F}$ , is a colourless, odourless gas, which does not solidify when cooled in liquid air and is insoluble in water, but alcohol dissolves four times, and acetone 5·5 times its own volume of the gas at  $20^\circ$ . It burns in air with a green edged flame. It is readily absorbed by bromine, fluorodibromoethane being formed. *Fluorodibromoethane*,  $\text{CHFBr}\cdot\text{CH}_2\text{Br}$ , boils at  $121\cdot5^\circ$ , has a sp. gr.  $2\cdot26333$  at  $10\cdot5^\circ$ , and  $n_D$   $1\cdot51235$ ,  $n_D$   $1\cdot51759$ , and  $n_H$   $1\cdot53278$  at  $10\cdot5^\circ$ . It crystallises at  $-55^\circ$ , and melts at  $-54^\circ$ .

When difluorobromoethane is heated with potassium hydroxide dissolved in ethyl alcohol, it yields difluorodiethyl ether and difluoroethylene. The yield of difluoroethylene in this case is 32 per cent. of the theoretical; if methyl alcohol is employed instead of ethyl alcohol, then the yield is 26 per cent., whereas with propyl alcohol it is 40 per

cent., and with amyl alcohol 61 per cent. In all cases, the corresponding difluoroether is also produced.

*Difluoroethylene*,  $\text{CF}_2\cdot\text{CH}_2$ , is a colourless, odourless gas of density 2.21, corresponding with a mol. wt. of 63.84, the calculated mol. wt. being 63.9. Alcohol or chloroform dissolves  $1\frac{1}{2}$  times its own volume of the gas. It neither polymerises nor oxidises when exposed to the air, and when cooled in liquid air, it solidifies to snow-like flakes. It readily absorbs bromine,  *$\alpha$ -difluorodibromoethane* being formed.

*$\alpha$ -Difluorodibromoethane*,  $\text{CF}_2\text{Br}\cdot\text{CH}_2\text{Br}$ , is a colourless liquid, boils at  $93^\circ$ , has a sp. gr. 2.4228 at  $12.2^\circ$ ,  $n_D^{20}$  1.44957,  $n_D^{25}$  1.45249,  $n_H^{20}$  1.46555 at  $12.2^\circ$ ; it solidifies at  $-58^\circ$  and melts at  $56.5^\circ$ .

*Difluorodiethyl ether*,  $\text{CHF}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_2\text{H}_5$ , is a very volatile, colourless liquid with an ethereal odour, is somewhat soluble in water, and has a sp. gr. 1.039 at  $15^\circ$ . It is oxidised by nitric acid or chromic mixture.

*Difluoroethyl methyl ether*,  $\text{CHF}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_3$ , boils at  $47^\circ$ ; 100 vols. of water dissolve 5 vols. of this compound. On oxidation with chromic mixture, it yields *difluoroacetic acid*. *Barium difluoroacetate* is very soluble in water, but almost insoluble in alcohol. It crystallises in star-like aggregates of slender needles.

*Difluoroethyl propyl ether* boils at  $89^\circ$ .

Since difluoroethyl methyl ether on oxidation gives difluoroacetic acid, it follows that it must contain the group  $\text{CHF}_2\cdot\text{CH}_2-$ , which must also be present in the difluorodiethyl ether.

*Difluoroiodoethane*,  $\text{C}_2\text{H}_3\text{IF}_2$ , produced by heating difluorobromoethane with calcium iodide in alcoholic solution, is a colourless liquid, boils at  $89.5^\circ$ , has a sp. gr. 2.24328 at  $12.2^\circ$ , and  $n_D^{20}$  1.46455,  $n_D^{25}$  1.46807, and  $n$  1.48467 at  $12.2^\circ$ . When oxidised with nitric acid, it yields difluoroacetic acid.

When tribromoethane is treated with a mixture of antimony trifluoride and bromine, both difluorobromoethane and fluorodibromoethane are produced. The fluorodibromoethane thus produced is in every way identical with that obtained by the action of bromine on fluoroethylene.

*Fluorobromoethylene*,  $\text{CH}_2\cdot\text{CBrF}$ , is obtained by the action of a mixture of potassium acetate and carbonate on fluorodibromoethane. It is a very volatile liquid boiling at  $30-33^\circ$ , and readily polymerises and oxidises on exposure to air (compare fluorobromoethylene,  $\text{CHBr}\cdot\text{CHF}$ , *Bull. Acad. Roy. Belg.*, 1897, [iii], 33, 456). H. R. LE S.

**Action of Normal Propyl and Butyl Alcohols on their respective Sodium Derivatives; Synthesis of Dipropyl and Dibutyl Alcohols.** By MARCEL GUERBET (*Compt. rend.*, 1901, 133, 1220—1222. Compare *Abstr.*, 1899, i, 471, 472; 1901, i, 182, 307, 625).—When propyl alcohol is heated under pressure for 24 hours at  $220-230^\circ$ , sodium propionate, propyl propionate, and a hexylic alcohol are formed; much hydrogen is produced during the operation. The hexylic alcohol is  $\beta$ -methylamyl alcohol (b. p.  $148^\circ$ ) being oxidised by chromic acid to  $\beta$ -methylvaleric acid (b. p.  $193.5^\circ$ ).

Under the same conditions, butyl alcohol yields corresponding products; the *octylic alcohol* (dibutyl alcohol),  $\text{C}_8\text{H}_{17}\cdot\text{OH}$ , obtained is a

colourless, oily liquid boiling at  $181^{\circ}$  under 758 mm. pressure, and has a sp. gr. 0.8483 at  $0^{\circ}$ . K. J. P. O.

**Preparation of Trichlorotert. butyl Alcohol.** By MARCEL GUÉDRAS (*Compt. rend.*, 1901, 133, 1011).—If a mixture of equal volumes of acetone and chloroform is allowed to drop on potassium hydroxide heated at  $30^{\circ}$ , and the mixture is afterwards heated at  $50^{\circ}$  for an hour, trichlorotert. butyl alcohol,  $\text{CCl}_3 \cdot \text{CMe}_2 \cdot \text{OH}$ , is formed, and can be isolated by distilling in steam, after removal of unaltered acetone and chloroform by heating at a temperature below  $70^{\circ}$ . It melts at  $80\text{--}81^{\circ}$ , boils at  $167^{\circ}$ , has a characteristic camphoraceous odour, is almost insoluble in cold water, but soluble in most organic solvents, and is not affected by dilute acids or alkalis. It produces local anæsthesia and has antiseptic properties. C. H. B.

**Fermentation Amyl Alcohol.** By GUSTAVE BEMONT (*Compt. rend.*, 1901, 133, 1222—1224).—A specimen of the amyl alcohol, obtained by repeated fractionation of commercial fusel oil, and representing one-third of the quantity of the latter, boiled at  $131\text{--}131.5^{\circ}$ , has a sp. gr. 0.8065 at  $16^{\circ}$  and  $[\alpha]_D - 0^{\circ}55.5'$ . On oxidation with chromic acid, it yields an active valeric acid which boils at  $175^{\circ}$  under 763 mm. pressure and has  $[\alpha]_D + 2^{\circ}31.3'$ . The alcohol is probably  $\alpha$ -methylbutyl alcohol, and the acid  $\alpha$ -methylbutyric acid. In the oxidation are also formed a valeraldehyde, which boils at  $92\text{--}93^{\circ}$  under 761 mm. pressure and has  $[\alpha]_D + 0^{\circ}22.7'$ , and an amyl valerate boiling at  $191\text{--}192^{\circ}$  under 743 mm. pressure, and having  $[\alpha]_D 3^{\circ}14.8'$ . K. J. P. O.

**Synthesis and Properties of *l*-Erythritol.** By LÉON MAQUENNE (*Ann. Chim. Phys.*, 1901, 24, [vii], 399—412).—A résumé of work already published (compare Abstr., 1900, i, 423, 472; 1901, i, 497). G. T. M.

**Esterification of Phosphorous Acid by Glycerol and Glycol.** By P. CARRÉ (*Compt. rend.*, 1901, 133, 882—884).—A glycerophosphorous acid having the formula  $\text{O}:\text{PH}(\text{OH})\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$  is obtained on warming glycerol with phosphorous acid; the second hydroxyl group of the acid is not esterified even when the alcohol is in excess. The limits of esterification with molecular proportions, at  $125^{\circ}$  under the ordinary pressure, is reached in 20—30 hours, 60.6 per cent. of the acid being converted into ester; prolonged heating lowers the percentage owing to the loss of glycerol by evaporation. The limit is reached more rapidly when the experiment is made at  $125^{\circ}$  under 15 mm. pressure, the time required being 10 hours.

Barium glycerophosphite,  $\text{Ba}(\text{C}_3\text{H}_9\text{O}_5\text{P})_2$ , is amorphous and very soluble; it is hydrolysed by boiling water and by cold solutions of the alkali hydroxides.

The acid,  $\text{O}:\text{PH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , results from the interaction of glycol and phosphorous acid; it is monobasic, its deliquescent barium salt having the composition  $\text{Ba}(\text{C}_2\text{H}_6\text{O}_4\text{P})_2$ . G. T. M.

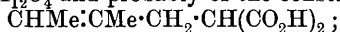
**New Volatile Beryllium Salt.** By G. URBAIN and H. LACOMBE (*Compt. rend.*, 1901, 133, 874—876).—The basic *beryllium acetate*,  $\text{Be}_4\text{O}(\text{OAc})_6$ , produced by dissolving the product of the action of dilute acetic acid on beryllium hydroxide in glacial acetic acid, separates from this solvent in needles or octahedral crystals insoluble in cold water and almost insoluble in alcohol or ether; it is decomposed by hot water. The salt crystallises best from chloroform, melts to a colourless liquid at  $283\text{--}284^\circ$ , and boils without decomposition at  $330\text{--}331^\circ$  under the ordinary pressure. The vapour may be superheated to  $360^\circ$  without undergoing any decomposition. The salt may even be heated at  $150^\circ$  in the presence of hydrochloric and glacial acetic acids without alteration. The vapour density of the compound determined by V. Meyer's method is additional evidence in favour of the bivalent character of beryllium.

G. T. M.

**Action of higher Aliphatic Acids on Normal Alkali Carbonates.** By J. KLIMONT (*J. pr. Chem.*, 1901, [ii], 64, 493—495).—The higher fatty acids (stearic, oleic, arachic) which are insoluble in water react with aqueous sodium carbonate, giving sodium hydrogen carbonate and the sodium salt of the fatty acid. With lower acids, which are somewhat soluble (decoic, &c.), the sodium hydrogen carbonate is also decomposed.

K. J. P. O.

**Action of Ethyl Sodiomalonate on Tribromides.** By WLADIMIR N. IPATIEFF and SWIDERSKI (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 532—540).—By the action of bromine, dimethylethylcarbinol yields a mixture of two dibromo-compounds,  $\text{CMe}_2\text{Br}\cdot\text{CHMeBr}$  and  $\text{CH}_2\text{Br}\cdot\text{CMeBr}\cdot\text{CH}_2\text{Me}$ , which, when further brominated, give two isomeric tribromoisopentanes of the constitution  $\text{CMe}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$  and  $\text{CH}_2\text{Br}\cdot\text{CMeBr}\cdot\text{CHMeBr}$ . On treating the mixed tribromo-derivatives (1 mol.) with three atomic proportions of sodium and ethyl malonate (3 mols.), the following compounds were obtained: (1) ethyl ethanetetra-carboxylate; (2) the *ethyl* ester of an unsaturated *acid* of the composition  $\text{C}_8\text{H}_{12}\text{O}_4$  and probably of the constitution



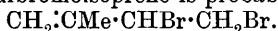
two fractions of the ethyl ester, boiling under 10 mm. pressure at  $115\text{--}120^\circ$  and  $120\text{--}124^\circ$ , have respectively the sp. gr. 1.058 and 1.064 at  $0^\circ/0^\circ$ ; (3) the ethyl ester of an unsaturated *bromo-acid*,  $\text{CMeBr}:\text{CMe}:\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})_2$ , which, after crystallisation from benzene, melts at  $115\text{--}117^\circ$ ; (4) an ester isomeric with (3) and corresponding with an *acid*,  $\text{CMe}_2:\text{CBr}:\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})_2$ , melting at  $157\text{--}158^\circ$ . Both these bromo-acids form insoluble *silver* and *calcium* salts.

T. H. P.

**Isoprenic Acid.** By WLADIMIR N. IPATIEFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 540—545).—The action of sodium ethoxide on dibromo-isoprene and ethyl malonate gives rise to an *ethyl* ester,  $\text{C}_{12}\text{H}_{18}\text{O}_4$ , which in an impure condition boils at  $125\text{--}128^\circ$  under 15 mm. pressure; it is a transparent liquid having a faint odour and combines with bromine, and decolorises 1 per cent. permanganate solution; it has a sp. gr. 1.0566 at  $0^\circ/0^\circ$  and  $n_D$  1.45041, the molecular refraction calcu-

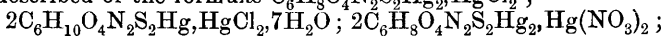
lated from this number showing that the molecule contains one double linking. On hydrolysis, the ester yields *isopropenyltrimethylenedicarboxylic acid* (*isoprenic acid*),  $\text{CH}_2:\text{CMe}\cdot\text{CH}\begin{matrix} \text{CH}_2 \\ | \\ \text{C}(\text{CO}_2\text{H})_2 \end{matrix}$ , which was obtained as an amorphous powder soluble in water or acetic acid; in freezing aqueous solution, the values 245, 233, and 314 were obtained for the molecular weight, so that the acid undergoes polymerisation; the acid melts and decomposes at about  $115^\circ$ , decolorises permanganate solution, and combines with bromine and hydrogen bromide, giving compounds not readily purified. The salts of the acid are mostly insoluble in water and amorphous; the *calcium* salt,  $\text{C}_8\text{H}_8\text{O}_4\text{Ca}\cdot 2\text{H}_2\text{O}$ , is obtained as a white, amorphous precipitate.

The composition of dibromoisoprene is probably



T. H. P.

**Cystin.** By JULIUS MAUTHNER (*Zeit. Biol.*, 1901, 42, 176—186).—Certain metallic compounds of cystin are described, particular attention being directed to that with copper, which is crystalline and has the formula  $\text{C}_6\text{H}_{10}\text{O}_4\text{N}_2\text{S}_2\text{Cu}$ . Cystin also forms a crystalline compound with hydrogen chloride,  $\text{C}_6\text{H}_{12}\text{O}_4\text{N}_2\text{S}_2\cdot 2\text{HCl}$ . Compounds are also described of the formulæ  $\text{C}_6\text{H}_8\text{O}_4\text{N}_2\text{S}_2\text{Hg}_2\cdot \text{HgCl}_2$ ;



Baumann (*Zeit. physiol. Chem.*, 8, 300) showed that cystin may be reduced to cystein by tin and hydrochloric acid and subsequent removal of the tin by hydrogen sulphide. It is now shown that hydrogen sulphide alone will bring about the same reduction.

W. D. H.

**Action of Fuming Sulphuric Acid on Acetaldehyde, Propaldehyde, and Acetone.** By MARCEL DELÉPINE (*Compt. rend.*, 1901, 133, 876—878).—The vapour of acetaldehyde, when passed into fuming sulphuric acid (50 per cent.  $\text{SO}_3$ ), yields acetaldehyde- $\beta\beta$ -disulphonic acid,  $\text{CHO}\cdot\text{CH}(\text{SO}_3\text{H})_2$ , and methanedisulphonic acid. The former acid yields, with aniline, *p*-toluidine and the naphthylamines, compounds of the type  $\text{CH}(\text{SO}_3\text{H})_2\cdot\text{CH}\cdot\text{NR}\cdot 2\text{H}_2\text{O}$ .

Propaldehyde, under these conditions, gives rise to propaldehyde- $\beta\beta$ -disulphonic acid,  $\text{CHO}\cdot\text{CMe}(\text{SO}_3\text{H})_2$ , the potassium salt of which, when heated with barium hydroxide solution, yields the corresponding salts of formic and ethylenedisulphonic acids.

Acetone also undergoes sulphonation, yielding *acetone- $\alpha\gamma$ -trisulphonic acid*,  $\text{SO}_3\text{H}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{SO}_3\text{H})_2$ , and the products of its hydrolysis, namely, disulphoacetic and methanedisulphonic acids. These acids were identified as barium salts. *Barium acetone- $\alpha\gamma$ -trisulphonate*,  $\text{Ba}_3[\text{C}_3\text{H}_3\text{O}(\text{SO}_3)_3]_2\cdot 2\text{H}_2\text{O}$ , when dried at  $105^\circ$ , is an amorphous substance resembling alumina or silica; it yields the corresponding salts of disulphoacetic and methanedisulphonic acids when boiled with barium hydroxide solution.

G. T. M.

**Electrolytic Production of Haloid Derivatives of Acetone.** By A. RICHARD (*Compt. rend.*, 1901, 133, 878—880).—Monochloroacetone is produced by electrolysis a mixture of hydrochloric acid and acetone. The best yield is obtained when the acetone is in excess

and the electrolysis conducted in a well-cooled electrolytic cell fitted with an anode having a large surface. The hydrogen evolved at the cathode has no action on the product.

Monobromoacetone is conveniently prepared by electrolysing a mixture of hydrobromic acid and acetone at 35—40°, but in this case the hydrogen must be evolved in a separate cathode cell, owing to its reducing action on the product. G. T. M.

**Action of Nitric Acid on Aliphatic Compounds containing the Group CH(OH).** I. Action of Nitric Acid on Secondary Alcohols. II. Action of Nitric Acid on Ketonic Alcohols,  $R \cdot CO \cdot CH(OH) \cdot R$ . By GIACOMO PONZIO (*Atti R. Accad. Sci. Torino*, 1900—1901, 36, 721—733).—The first part of this paper has been already abstracted (see Abstr., 1901, i, 477).

The action of nitric acid of sp. gr. 1.37 on ketonic alcohols,  $R \cdot CO \cdot CHR \cdot OH$  ( $\alpha$ -ketoles or aliphatic benzoin), affords a convenient means of preparing symmetrical  $\alpha$ -diketones of the aliphatic series. The following compounds have been obtained in this way.

Dipropionyl, prepared from propioin,  $[CH_2Me \cdot CO \cdot CH(OH) \cdot CH_2Me]$ , was distilled in a current of steam and converted into its *dioxime*,  $C_8H_{12}O_2N_2$ ; this crystallises from benzene in shining, white needles which melt and sublime at 185°, and are soluble in water, alcohol, chloroform, ether, or light petroleum.

*Dibutyryl*,  $CH_3Et \cdot CO \cdot CO \cdot CH_2Et$ , obtained together with dinitropropane by the oxidation of butyrolin, is a yellow oil. The *dioxime*,  $C_8H_{16}O_2N_2$ , separates from benzene in slender, shining needles melting at 175°, and dissolving in alcohol, ether, or chloroform.

*Diisobutyryl*,  $CHMe_2 \cdot CO \cdot CO \cdot CHMe_2$ , obtained from *isobutyrolin*, gives a *dioxime*,  $C_8H_{16}O_2N_2$ , which crystallises from benzene in white needles melting and subliming at 163—164° and dissolving in alcohol or ether.

*Diisovaleryl*,  $CHMe_2 \cdot CH_2 \cdot CO \cdot CO \cdot CH_2 \cdot CHMe_2$ , prepared from *isovaleroin*, yields a *dioxime*,  $C_{10}H_{20}O_2N_2$ , separating from benzene in shining, white needles which melt and sublime at 195°; it is soluble in alcohol, ether, or chloroform. T. H. P.

**Synthetical Experiments with Tetra-acetylchlorodextrose and Tetra-acetylchlorogalactose.** By ZDENKO H. SKRAUP and R. KREMANN (*Monatsh.*, 1901, 22, 1037—1048).—Investigation of the action of phenylhydrazine on tetra-acetylchlorodextrose has resulted in the isolation of glucosazone only, in addition to acetylphenylhydrazine and phenylhydrazine hydrochloride.

Attempts to synthesise a disaccharide by the action of tetra-acetylchlorodextrose on the sodium and lead derivatives of dextrose were unsuccessful. A small amount of  $\beta$ -penta-acetyldextrose (m. p. 112°) was formed from tetra-acetylchlorodextrose on boiling it with molecular silver in toluene. When heated with metallic sodium and finely divided silver nitrate in ether, tetra-acetylchlorodextrose was converted into *tetra-acetylnitrodextrose* which melted at 92°. This, when heated with sodium acetate and glacial acetic acid, yielded  $\alpha$ -penta-acetyldextrose (m. p. 132°). On recrystallisation from alcohol, the almost



inactive tetra-acetylnitrodextrose ( $[\alpha]_D + 1.536^\circ$ ) became active ( $[\alpha]_D + 143.65^\circ$  at  $25^\circ$ ) and melted at  $145^\circ$ . This is probably the tetra-acetylnitrodextrose previously described by Colley and Königs (m. p.  $151^\circ$ ;  $[\alpha]_D + 149.16^\circ$  at  $18^\circ$ ).

When boiled with metallic sodium and silver nitrate, in ether, tetra-acetylchlorogalactose exchanges the chlorine atom for hydroxyl, yielding *tetra-acetylgalactose*. This melts at  $145^\circ$ , and has  $[\alpha]_D + 137.17^\circ$  at  $25^\circ$ . When boiled with sodium acetate and acetic anhydride, it is converted into penta-acetylgalactose (m. p.  $142^\circ$ ). By hydrolysis of the tetra-acetylgalactose and subsequent treatment with phenylhydrazine, glucosazone was obtained. G. Y.

**Hepta-acetylmaltose Nitrate (Acetonitromaltose) and Hepta-acetyl- $\beta$ -methylmaltoside.** By WILHELM KOENIGS and EDUARD KNORR (*Ber.*, 1901, 34, 4343—4348. Compare Abstr., 1901, i, 369).—*Hepta-acetylmaltose nitrate*,  $C_{12}H_{14}O_3(OAc)_7 \cdot NO_3$ , is prepared by treating octoacetylmaltose with an ice-cold mixture of chloroform and fuming nitric acid; it crystallises in large prisms melting at  $93$ – $95^\circ$  and has  $[\alpha]_D + 149.18'$  at  $19^\circ$ . On boiling the nitrate with methyl alcohol in the presence of barium carbonate and a few drops of pyridine, hepta-acetylmethylmaltoside is formed; this melts at  $128$ – $129^\circ$ , and has  $[\alpha]_D + 60.46'$  at  $20^\circ$  (compare Fischer and Armstrong, Abstr., 1901, i, 671). On hydrolysis with barium hydroxide,  $\beta$ -methylmaltoside is obtained, forming colourless needles melting at  $93$ – $95^\circ$  and decomposing at  $100^\circ$ ; fermentation converted it into  $\beta$ -methylglucoside.

Pure octoacetylsucrose can be quantitatively hydrolysed when it is treated with a cold solution of sodium hydroxide in aqueous methyl alcohol for a few hours. K. J. P. O.

**Cellobiose.** By ZDENKO H. SKRAUP and J. KÖNIG (*Monatsh.*, 1901, 22, 1011—1036. See Abstr., 1901, i, 370).—The name *cellobiose* is now used for the substance previously termed *cellose*. Cellobiose, on hydrolysis by dilute sulphuric acid, is shown to yield dextrose only. Cellobiose forms a *phenylhydrazone* which decomposes at  $90^\circ$  and an *osazone* which melts at  $198^\circ$ .

*Hepta-acetylchlorocellobiose*,  $C_{26}H_{35}O_{18}Cl$ , is formed by the action of hydrogen chloride on the solution of heptaacetylcellobiose in acetic anhydride. It forms small needles which melt at  $178^\circ$ .

*Hepta-acetylmethylcellobioside* is formed by shaking with silver carbonate hepta-acetylchlorocellobiose in methyl alcohol solution; it crystallises from alcohol in white needles melting at  $173^\circ$ , and on hydrolysis yields a substance which closely resembles cellobiose but may be methylcellobioside.

Attempts to obtain cellobiose from sprouting beans were unsuccessful. G. Y.

**Acetylation of Soluble Starch.** By FRITZ PREGL (*Monatsh.*, 1901, 22, 1049—1066).—Soluble starch prepared by Zulkowsky's method yielded, on acetylation by acetic anhydride in presence of a small quantity of sulphuric acid in the cold, an amorphous *triacetyl*

derivative,  $C_6H_7O_5Ac_3$ , which did not reduce copper or bismuth salts, and was not coloured by iodine. It sintered at  $260^\circ$ , decomposed at  $275^\circ$ , and had  $[\alpha]_D$   $163.6^\circ$ . Molecular weight determinations showed the molecular weight to be from eight to nine times that corresponding with the empirical formula. The product obtained on hydrolysis of the acetyl derivative was identical with the soluble starch and had  $[\alpha]_D$   $+191.73^\circ$  at  $20^\circ$ . Soluble starch had  $[\alpha]_D$   $+191.27^\circ$  at  $20^\circ$ . On analysis, both gave the formula  $C_6H_{10}O_5$  (compare Syniewski, Abstr., 1898, i, 61).

Acetylation with an increased amount of sulphuric acid yielded a product having the empirical formula  $C_6H_7O_5Ac_3$ ; the molecular weight determinations showed, however, that this formula must be tripled. This acetyl compound is soluble in alcohol, melts at  $150$ — $155^\circ$ , has  $[\alpha]_D$   $149.03^\circ$ , and reduces alkaline copper solutions. Hydrolysis yielded a dextrin which gave a red coloration with iodine, had  $[\alpha]_D$   $+187.0^\circ$ , and could not be identified with any dextrin previously described. G. Y.

**Humic Substances.** By FAUSTO SESTINI (*L'Orosi*, 1901, 24, 289—299).—The humic substances which have been previously described by various authors must not be considered as so many different modifications of one individual substance, since facts are not lacking which indicate marked differences in properties between humic substances from divers sources. Artificial humic matter prepared from non-nitrogenous compounds contains no trace of nitrogen, whilst that obtained from the humus of the soil retains tenaciously a certain quantity of nitrogenous material. The author applies Liebermann's theory of colour shade (Abstr., 1901, ii, 368) to the change of colour from black to red and afterwards to yellow when humic substances are oxidised and nitrated; also to the case of sacculmic acid which changes from brown to yellow when a portion of its hydroxyl is replaced by bromine, whilst the black colour returns if the hydroxyl is restored to the compound. The influence of the methoxy-group on the colour of organic compounds, which was pointed out by Liebermann (*loc. cit.*), is probably exerted in the case of humic substances, the author having often detected an odour of chloroform, bromoform, or methyl esters on treating such substances with chlorine or bromine. By oxidation and nitration with concentrated nitric acid (sp. gr. 1.4), the molecule of humic substances is quickly destroyed with the formation of a mixture of products among which are nitration products belonging to the aromatic series; the only aromatic group which has been identified is the benzene nucleus. Quinone readily undergoes change into a black mass, which is also formed at the ordinary temperature from an aqueous solution of quinone kept in the dark and in an atmosphere of carbon dioxide; it is probable that an additive product of quinone with water is first formed, and that this is gradually decomposed between  $15^\circ$  and  $95^\circ$  into quinol and black matter by the action of the liberated oxygen. The author confirms the views previously put forward by him that ulmin and sacculmin cannot be regarded as merely mixtures of the potassium salts of humic acids. As regards

the chemical functions of humic substances, it is probable that beside anhydride or ether-linkings they contain ketonic, hydroxyl, and alkyl groups, partly arranged in open, and partly in closed, chains.

T. H. P.

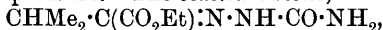
**Birotation of Chitosamine (Glucosamine).** By ERNST EDW. SUNDVIK (*Zeit. physiol. Chem.*, 1901, 34, 157).—At a low temperature, a solution of glucosamine hydrochloride shows a rotation of  $24.5^\circ$ . After heating for an hour and then cooling to the same temperature, the rotation is only  $18^\circ$ .

W. D. H.

**Action of Monoamino-acids on Phosphotungstic Acid.** By ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1901, 33, 574—578. Compare Kossel and Kutscher, *Abstr.*, 1901, i, 107).—A solution of pure phosphotungstic acid does not precipitate glycine, leucine, aminovaleric acid, or tyrosine from 5 per cent. solutions. Phenylaniline is, however, partially or wholly precipitated. It is probable that in the presence of other substances the amino-acids may be precipitated. The precipitates obtained in the investigation on histone bases (this vol., i, 193) gave negative results when tested for amino-acids.

J. J. S.

**Action of Dilute Mineral Acids on Ethyl Aminodimethyl Acrylate.** By LOUIS BOUVEAULT and A. WAHL (*Bull. Soc. Chim.*, 1901, [iii], 25, 1031—1040).—When heated with dilute mineral acids, ethyl aminodimethylacrylate,  $\text{CMe}_2\cdot\text{C}(\text{NH}_2)\cdot\text{CO}_2\text{Et}$ , is converted into *ethyl dimethylpyruvate*,  $\text{CHMe}_2\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ , which forms a mobile, colourless, ethereal liquid and boils at  $64\text{--}69^\circ$  under 35 mm. or at  $60^\circ$  under 10 mm. pressure. The *semicarbazone*,



separates in needles from a mixture of ether and light petroleum and melts at  $95\text{--}96^\circ$ . The *oxime*,  $\text{CHMe}_2\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{NOH}$ , crystallises in needles from a mixture of ether and light petroleum and melts at  $57^\circ$ .

*Dimethylpyruvic acid*,  $\text{CHMe}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , distils at  $65\text{--}67^\circ$  under 10 mm. pressure, forms colourless leaflets, and melts at  $31^\circ$ ; its *oxime* forms white crystals and melts and decomposes at  $163\text{--}165^\circ$ ; the *phenylhydrazone* separates from aqueous methyl alcohol in yellow needles often several centimetres long, and melts at  $156\text{--}157^\circ$  without decomposition. The acid is reduced by sodium amalgam and alcohol to  $\alpha$ -hydroxyisovaleric acid; by the action of ammonia on the ester, dimethylpyruvamide (Moritz, *Trans.*, 1880, 35, 14) is produced. Dimethylpyruvic acid has been prepared in an impure state by Moritz (*loc. cit.*), by Brunner (*Abstr.*, 1895, i, 335), who describes a silver salt and a diphenylhydrazone melting at  $129^\circ$ , and by Kohn (*Abstr.*, 1899, i, 328), who describes an oxime melting at  $102^\circ$  and a phenylhydrazone melting at  $137^\circ$ , but the products obtained differ substantially from those here described.

T. M. L.

**Thiocyanogen, the so-called  $\psi$ -Thiocyanogen, and the Yellow Colouring Matter obtained from Thiocyanates.** By ALWIN GOLDBERG (*J. pr. Chem.*, 1901, [ii], 64, 439—470. Compare *Abstr.*, 1901, i, 516, 677).—Analyses of commercial canarin show that it has

the formula  $C_8H_6ON_8S_7$  (*loc. cit.*). The decomposition of canarin by water, alkalis, concentrated acids, and heat is studied. Metallic compounds with sodium, potassium, copper, zinc, silver, and magnesium are described.

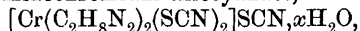
The yellow substance which is formed as a bye-product in the preparation of the dye canarin is contained in the mother liquors, from which the sodium salt of canarin has separated, and has the formula  $C_8H_4ON_4S_2$  (?). The relation of the yellow substance to canarin is discussed, and constitutional formulæ are suggested for both substances.

K. J. P. O.

**New Methods for the Preparation of Dithiocyanochromium Salts.** By PAUL PFEIFFER (*Ber.*, 1901, 34, 4303—4307. Compare Abstr., 1900, i, 688).—Dithiocyanodiethylenediaminechromium thiocyanate (*loc. cit.*) may be obtained when potassium chromothiocyanate,  $K_3CrS_6C_6N_6$ , is heated with anhydrous ethylenediamine for three hours on the water-bath. The yield is small as part undergoes decomposition during purification by crystallisation from water. When this salt is heated with ethylenediamine, it is partially transformed into the luteo-salt,  $Cr(C_2H_8N_2)_3(SCN)_3$ , as also is potassium chromothiocyanate.

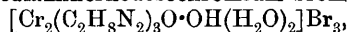
J. J. S.

**Chromammonium Compounds. II.** By PAUL PFEIFFER (*Zeit. anorg. Chem.*, 1901, 29, 107—137. Compare Abstr., 1900, i, 559; 1901, ii, 659).—*Dithiocyanodiethylenediaminechromium salts.* Dithiocyanodiethylenediaminechromium thiocyanate,



was obtained in prismatic needles from the salt  $[Cr(C_2H_8N_2)_3]Cl_3$  by first preparing the luteothiocyanate  $[Cr(C_2H_8N_2)_3](SCN)_3 \cdot H_2O$ ; then heating this at  $130^\circ$ , when it loses ethylenediamine and water, and finally extracting with water and crystallising. The salt is easily soluble in pyridine and in sulphuric acid, but is decomposed by heating with water. The chloride,  $[Cr(C_2H_8N_2)_2(SCN)_2]Cl \cdot H_2O$ , is obtained in orange-yellow needles by treating the thiocyanate with concentrated hydrochloric acid. By treatment with hydrobromic acid, nitric acid, and sulphuric acid, the *bromide*, with  $\frac{1}{2}H_2O$ , the *nitrate*, with  $1H_2O$ , and the *hydrogen sulphate*, with  $1\frac{1}{2}H_2O$ , have been obtained, besides an acid chloride the composition of which appears to be variable.

*Ethylenediaminerhodoso chromium salts.* In the preparation of the luteochloride some rhodoso salt is also formed and is most easily isolated as ethylenediaminerhodoso chromium bromide,



which is obtained in transparent, red crystals. It is soluble in water and with potassium thiocyanate gives the thiocyanate.

The molecular weights of the luteoethylenediaminechromium salts, and the thiocyno-compounds described were determined by the cryoscopic method.

J. McC.

**Formation of Carbamide from Nitrogenous Substances.** By JOHANN PLOT (*Chem. Centr.*, 1901, ii, 1335—1336; from *Oesterr. Chem. Zeit.*, 4, 485—487. Compare Jolles, Abstr., 1900, ii, 636; 1901, i, 30, 262, 583; this vol., i, 86).—In opposition to Jolles, the

author considers that in the oxidation of purine compounds it is not the group  $\text{CO}\cdot\text{NH}_2$  existing in these compounds which yields carbamide, but rather that the formation of carbamide results from the union of the decomposition products, ammonia and carbon dioxide, in presence of nascent carbonic acid ( $\text{H}_2\text{CO}_3$ ).  
E. W. W.

**Isomerism in the Hydroxyureas.** By LUIGI FRANCESCONI and A. PARROZZANI (*Gazzetta*, 1901, 31, ii, 334—347).—The action of hydroxylamine on potassium cyanate yields, in addition to the hydroxycarbamide described by Dresler and Stein (*Annalen*, 1869, 150, 242), an isomeric compound to which the authors give the name

*isohydroxycarbamide* and the constitution  $\begin{array}{c} \text{OH}\cdot\text{C}\cdot\text{NH}_2 \\ | \\ \text{N}\cdot\text{OH} \end{array}$ . This compound and hydroxycarbamide (which is probably first produced in its tautomeric form having the structure  $\begin{array}{c} \text{OH}\cdot\text{C}\cdot\text{NH}_2 \\ | \\ \text{OH}\cdot\text{N} \end{array}$  and then passes into

the compound having the ordinary formula,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$ ), are supposed to owe their formation to the fact that cyanic acid takes part in the reaction with hydroxylamine in its two tautomeric forms. This explanation is borne out by the observation that in the condensation of cyanic acid or of esters of *isocyanic* acid with phenylhydroxylamine, no stereoisomerides are obtained, whilst in the action of esters of *isocyanic* acid on hydroxylamine, derivatives of *isohydroxycarbamide* seem to be produced although they have not as yet been isolated.

*isohydroxycarbamide*,  $\text{CH}_4\text{O}_2\text{N}_2$ , crystallises from ether in iridescent plates melting at  $70\text{--}72^\circ$  and completely decomposing into water, carbon dioxide, ammonia, and nitrogen, and is readily soluble in water, from which it is deposited unaltered; it is readily soluble in alcohol, moderately so in ether, and reduces Fehling's solution in the cold. With ferric chloride, it gives a transitory red coloration quite different from the blue colour obtained with hydroxycarbamide, into which it is transformed on heating in alcoholic solution. By boiling water, it is decomposed, with evolution of ammonia, into hydroxycarbamide and a substance giving a cherry-red coloration with ferric chloride. It has the normal molecular weight in freezing aqueous solution. Its *hydrochloride* separates in large, rectangular prisms which reduce Fehling's solution in the cold, and give a transitory rose-red coloration with ferric chloride; it is stable in a vacuum at the ordinary temperature. The *diacetyl* derivative,  $\text{C}_5\text{H}_8\text{O}_4\text{N}_2$ , crystallises from ether in mammillary masses, which melt at  $105\text{--}106^\circ$ , dissolve readily in alcohol, and give no reaction either with ferric chloride or with Fehling's solution; it has the normal molecular weight in freezing water, and when its aqueous solution is evaporated to dryness in a vacuum, a viscous residue remains which colours ferric chloride an intense red.

*Potassium oxyfulminate*,  $\text{CO}_2\text{NK}$ , obtained by the action of potassium hydroxide on *isohydroxycarbamide* in absolute alcoholic solution, crystallises in needles which, with ferric chloride, give an intense blood-red coloration quickly changing to yellow; it reduces Fehling's solution on heating, and its aqueous solution evolves carbon dioxide on addition of hydrochloric acid; with silver nitrate, it gives a white, and with mercuric chloride a yellow, precipitate, both of which rapidly

blacken. The electrical conductivity was determined,  $\mu$  varying from 141.7 for a dilution  $V=32$  to 159.9 for  $V=1024$ .

*Methylhydroxycarbamide*,  $\text{OH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHMe}$ , prepared from methylcarbimide and hydroxylamine, crystallises from ethyl acetate in rhomboidal plates melting and decomposing at  $127^\circ$  and is very soluble in water, less so in methyl and ethyl alcohols, and slightly in ether; it gives the characteristic bluish-violet coloration with ferric chloride and reduces Fehling's solution. No other compound could be isolated from the products of the reaction yielding methylhydroxycarbamide, but after the separation of the latter a viscous substance remained which, with ferric chloride, gave a rose-red coloration.

*Ethylhydroxycarbamide*,  $\text{OH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHEt}$ , melts and decomposes at  $129^\circ$ , and is soluble in water and in methyl or ethyl alcohol.

*Phenylhydroxycarbamide*,  $\text{OH}\cdot\text{NPh}\cdot\text{CO}\cdot\text{NH}_2$ , prepared by the action of hydrochloric acid on a mixture of phenylhydroxylamine and potassium cyanate, melts at  $95^\circ$ , is soluble in nearly all solvents, and gives with ferric chloride a dark bluish-violet coloration. Its *hydrochloride* is a white, crystalline, very deliquescent compound melting and decomposing at  $90^\circ$ .

*Phenylmethylhydroxycarbamide*,  $\text{OH}\cdot\text{NPh}\cdot\text{CO}\cdot\text{NHMe}$ , prepared from methyl carbimide and phenylhydroxylamine, crystallises from benzene in mammillary aggregates of needles melting at  $121^\circ$ . Its *hydrochloride* separates in unstable acicular crystals which lose hydrogen chloride at  $100^\circ$ .

*Phenylethylhydroxycarbamide*,  $\text{OH}\cdot\text{NPh}\cdot\text{CO}\cdot\text{NHEt}$ , crystallises from a mixture of benzene and ether in mammillary groups of needles melting at  $93^\circ$ . Its *hydrochloride* is unstable, and crystallises with difficulty.

The authors give details of improvements on Erdmann's method for preparing potassium cyanate (Abstr., 1894, i, 2). T. H. P.

**New Oxidation Product of Uric Acid.** By MAX SCHOLTZ (*Ber.*, 1901, 34, 4130—4132).—*Tetracarbimide*,  $\text{OC} \begin{array}{c} \text{NH}\cdot\text{CO}\cdot\text{NH} \\ \text{NH}\cdot\text{CO}\cdot\text{NH} \end{array} \text{CO}$ , is produced by oxidising sodium urate, dissolved in water, with a 3 per cent. solution of hydrogen peroxide, the reaction being accelerated by gently warming; the yield of this compound is only about 10 per cent. of the uric acid taken. The new product has no definite melting point but when heated evolves a pungent vapour which reddens lacmoid paper; it is insoluble in cold water and the ordinary organic solvents, but dissolves in hot water and sodium hydroxide solution. The *sodium* salt,  $\text{C}_4\text{H}_2\text{O}_4\text{N}_4\text{Na}$ , is very soluble in water but insoluble in alcohol. The *barium* salt,  $\text{C}_4\text{Ba}_2\text{O}_4\text{N}_4$ , is obtained as a crystalline precipitate by mixing hot solutions of tetracarbimide and barium hydroxide. The *calcium*, *silver*, *lead*, and *copper* salts are insoluble, the first two being amorphous whilst the others are crystalline.

G. T. M.

**Chloroimides.** By JOSEPH TSCHERNIAC [with A. BRAUN] (*Ber.*, 1901, 34, 4209—4214).—The chloroimides of phthalic and succinic acids, when boiled with water, yield the imides and the acids together with

nitrogen and chlorine, but no hypochlorous acid ; neither is hypochlorous acid formed by the action of cold water on the chloroimides. The oxidising and bleaching properties of an aqueous solution of succinochloroimide are therefore due to the chlorine liberated.

R. H. P

**Adiponitrile.** By LOUIS HENRY (*Bull. Acad. Roy. Belg.*, 1901, 7, 367—372. Compare Abstr., 1886, 786, 860).—*Adiponitrile* (aa-di-cyanobutane),  $C_4H_8(CN)_2$ , obtained by the action of potassium cyanide on tetramethylene dibromide or di-iodide, is a thick, colourless, odourless liquid having a bitter taste ; it boils at  $295^\circ$  under 760 mm. pressure, has a sp. gr. 0.951 at  $19^\circ/19^\circ$ , and  $n_D$  1.4397 ; the molecular refraction is 29.85, the calculated value being 29.70. When strongly cooled, it solidifies to a mass of long, needle-shaped crystals which melt at  $0^\circ$  to  $1^\circ$ . It readily combines with hydrogen bromide to form a white, crystalline mass, and on hydrolysis yields adipic acid. A review of the melting points of the dinitriles of the acids of the succinic series shows that those nitriles with an uneven number of carbon atoms melt at a lower temperature than those with an even number.

H. R. LE S.

**Hydrazide and Azide [Azoimide] of Propionic and iso-Valeric Acids.** By HERMANN HILLE (*J. pr. Chem.*, 1901, [ii], 64, 401—418).—*Propionylhydrazide*,  $CH_3Me \cdot CO \cdot N_2H_3$ , prepared by boiling hydrazine hydrate with ethyl propionate and fractionating the product under reduced pressure, is an extremely hygroscopic solid melting at  $40^\circ$  and boiling at  $130^\circ$  under 16 mm. pressure ; it reduces an ammoniacal solution of silver, and Fehling's solution ; the *hydrochloride* forms a white, crystalline solid, melting and decomposing at  $150^\circ$ . *Propionylbenzylidenehydrazide*,  $CH_3Me \cdot CO \cdot N_2H \cdot CHPh$ , prepared by the action of benzaldehyde on the hydrazide, crystallises in plates melting at  $115^\circ$ . *Propionyl-o-hydroxybenzylidenehydrazide*,  $CH_3Me \cdot CO \cdot N_2H \cdot CH \cdot C_6H_4 \cdot OH$ , crystallises in prisms melting at  $184^\circ$  ; *propionyl- $\beta$ -propylidenehydrazide*,  $CH_3Me \cdot CO \cdot N_2H \cdot CMe_2$ , forms prisms melting at  $101^\circ$ . *s-Dipropionylhydrazide*,  $N_2H_3(CO \cdot CH_2Me)_2$ , prepared by long boiling of propionic anhydride and hydrazine hydrate, or by heating propionylhydrazide and propionic anhydride under pressure at  $120^\circ$ , crystallises in plates melting at  $136^\circ$  and boiling at  $215$ — $217^\circ$  under 25 mm. pressure.

*Propionylazoimide* (propionylazide),  $CH_3Me \cdot CO \cdot N_3$ , prepared from propionylhydrazide hydrochloride and sodium nitrite, is an oil of disagreeable and irritating odour, readily volatile in ether vapour ; with absolute alcohol, it yields ethylurethane ; and with 50 per cent. alcohol, diethylcarbamide (m. p.  $108^\circ$ ) ; from the latter, by heating with concentrated hydrochloric acid, ethylamine hydrochloride is obtained (m. p.  $109^\circ$ ).

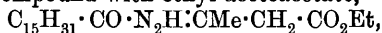
*isoValerylhydrazide*,  $CHMe_2 \cdot CH_2 \cdot CO \cdot N_2H_3$ , prepared from ethyl *isovalerate* and hydrazine hydrate, crystallises in hygroscopic scales or needles melting at  $68^\circ$  and boils at  $133^\circ$  under 15 mm. pressure ; the *hydrochloride* is crystalline, and melts and decomposes at  $174^\circ$  ; *isoValerylbenzylidenehydrazide*  $CHMe_2 \cdot CH_2 \cdot CO \cdot N_2H \cdot CHPh$ , crystallises in small plates melting at  $95^\circ$ . *isoValeryl-o-hydroxybenzylidenehydrazide* crystallises in needles melting at  $112^\circ$ . *isoValeryl- $\beta$ -propylidenehydrazide*,

$\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{N}_2\text{H} \cdot \text{CMe}_2$ , crystallises in small plates melting at  $67^\circ$ .

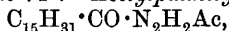
*s-Divalerylhydrazide*,  $\text{N}_2\text{H}_2(\text{CO} \cdot \text{CH}_2 \cdot \text{CHMe}_2)_2$ , is prepared by treating the monohydrazide in alcoholic solution with iodine and crystallises in long, prismatic plates melting at  $182^\circ$ .

*isoValerylazoimide*,  $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{N}_3$ , prepared by the action of sodium nitrite on valerylhydrazide hydrochloride, is an unstable, colourless solid which, on boiling with absolute alcohol, yields *isobutylurethane* (b. p.  $99^\circ$  under 19 mm. pressure), and with 50 per cent. alcohol, *s-diisobutylcarbamide* (m. p.  $128^\circ$ ). K. J. P. O.

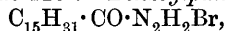
**Hydrazide and Azide [Azoimide] of Palmitic Acid.** By F. H. DELLSCHAFT (*J. pr. Chem.*, 1901, [ii], 64, 419—438).—*Palmitylhydrazide*,  $\text{C}_{15}\text{H}_{31}\text{CO} \cdot \text{N}_2\text{H}_2$ , prepared by adding ethyl palmitate to hydrazine hydrate, crystallises in needles melting at  $111^\circ$ ; the *hydrochloride* forms small needles melting at  $138$ — $143^\circ$ . *Palmitylbenzylidenehydrazide*,  $\text{C}_{15}\text{H}_{31} \cdot \text{CO} \cdot \text{N}_2\text{H} \cdot \text{CHPh}$ , prepared from the hydrazide and benzaldehyde, crystallises in microscopic needles melting at  $78^\circ$ . *Palmityl o-hydroxybenzylidenehydrazide* is a crystalline solid melting at  $104^\circ$ , and the compound with ethyl acetoacetate,



prepared from the hydrazide and ethyl acetoacetate, crystallises in small, white needles, which become soft and yellow at  $79^\circ$  and finally melt at  $122^\circ$ . *Palmityl- $\beta$ -propylidenehydrazide*,  $\text{C}_{15}\text{H}_{31} \cdot \text{CO} \cdot \text{N}_2\text{H} \cdot \text{CMe}_2$ , prepared from the hydrazide and acetone, forms microscopic, crystalline needles which melt at  $71^\circ$ . *Acetylpalmitylhydrazide*,



prepared by boiling the hydrazide with acetic anhydride, crystallises in small needles melting at  $129^\circ$ . *Benzoylpalmitylhydrazide*,



prepared by warming the hydrazide with benzoyl chloride, crystallises in microscopic needles which soften at  $100^\circ$  and melt at  $108^\circ$ . *Palmitylhydrindylhydrazide*,  $\text{C}_{15}\text{H}_{31} \cdot \text{CO} \cdot \text{N}_2\text{H} \cdot \text{CH} \cdot \text{C}_9\text{H}_9$ , prepared from hydrindaldehyde and the hydrazide, crystallises in white needles melting at  $86^\circ$ .

*s-Dipalmitylhydrazide*,  $\text{N}_2\text{H}_2(\text{CO} \cdot \text{C}_{15}\text{H}_{31})_2$ , prepared by the action of iodine on an alcoholic solution of the hydrazide, crystallises in small, insoluble needles melting at  $147^\circ$ .

*Palmitylazoimide*,  $\text{C}_{15}\text{H}_{31} \cdot \text{CO} \cdot \text{N}_3$ , prepared by the action of nitrous acid (nitrous fumes) on the hydrazide hydrochloride, forms crystals melting at  $49^\circ$  and decomposing at  $60^\circ$ . With absolute alcohol, pentadecylethylurethane (m. p.  $51^\circ$ ) is formed; with boiling water, *s-di-pentadecylcarbamide* (m. p.  $110^\circ$ ); with aniline, palmitylanilide (m. p.  $87.5^\circ$ ), and with ammonia, palmitylamide. Pentadecylamine is obtained when the urethane is boiled with concentrated hydrochloric acid; the amine yields insoluble compounds with mercuric and cadmium chlorides. K. J. P. O.

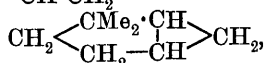
**Mixed Organo-magnesium Compounds and their Application to the Synthesis of Acids, Alcohols, and Hydrocarbons.** By VICTOR GRIGNARD (*Ann. Chim. Phys.*, 1901, 24, [vii], 433—490).—A



*résumé* of work already published (compare Abstr., 1900, i, 382; 1901, i, 250, 316, 393, 679). G. T. M.

**Dimethylhexamethylene from Camphoric Acid.** By NICOLAI D. ZELINSKY and N. LEPESCHKIN (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 549—565).—It has been previously shown (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 407) by the authors that from *isolaurene* a hydrocarbon,  $C_8H_{16}$ , can be obtained which, from its physical properties, must be a hexamethylene derivative. This compound, to which the name dihydro-*isolaurene* is given, the authors have now prepared by the following four methods: (1) By the action of concentrated hydriodic acid on *isolaurene* at  $200^\circ$ . (2) By the reduction of the liquid *isolaurene* hydriodide (see below) by means of hydrogen in presence of a zinc-palladium couple (see Abstr., 1899, i, 181). (3) By the action of concentrated sulphuric acid on *isolaurene*. (4) By the reduction of laurene hydriodide by means of hydrogen in presence of a zinc-palladium couple. As obtained by these different methods, dihydro-*isolaurene* has slightly varying properties, due probably to small quantities of impurities difficult to remove. The product yielded by method (1) is a pleasant smelling liquid boiling at  $114^\circ$  (corr.) and having the sp. gr.  $0.7686$  at  $17^\circ/4^\circ$ ,  $n_D$   $1.4223$  at  $17^\circ$ , and the molecular refraction (Lorentz and Lorenz' formula)  $37.05$ , the number calculated from the structural formula given below being  $36.82$ . The authors conclude that dihydro-*isolaurene* is a dimethylhexamethylene, and as the *o*-, *m*-, and *p*-dimethylhexamethylenes have been already prepared and characterised, it must be 1:1-dimethylhexamethylene,  $CH_2 \begin{smallmatrix} \diagup CH_2 \cdot CH_2 \\ \diagdown CH_2 \cdot CH_2 \end{smallmatrix} CMe_2$ . To *isolaurene*

the constitution  $\begin{smallmatrix} CMe_2 \cdot CH \cdot CH_2 \\ | \\ CH_2 - CH \cdot CH_2 \end{smallmatrix}$  is given and to laurene,



which would explain the ready conversion of its hydriodide into dimethylhexamethylene by reduction; the fact that the carbon-atom rings in laurene and in its hydriodide are identical is shown by the action of dimethylaniline on the latter compound, by which means laurene is reformed. It is probable that camphoric acid, which readily gives up carbon dioxide with the formation of laurene, also contains a six carbon atom ring.

When *isolaurene* or its hydrobromide is heated with concentrated hydrobromic acid in a sealed tube, a colourless, liquid, isomeric *hydrobromide* is obtained which boils at  $70$ — $71^\circ$  under  $15$  mm. pressure, and slowly decomposes on keeping. The liquid *hydriodide* obtained in a similar manner is faintly coloured, and boils at  $75$ — $80^\circ$  under  $15$ — $17$  mm. pressure. On heating *isolaurene* hydriodide with diethylaniline, *isolaurene* is obtained.

The action of concentrated sulphuric acid on *isolaurene* yields dihydro-*isolaurene* and a mobile *liquid* having the empirical composition  $C_8H_{13}$ , and boiling at  $259$ — $260^\circ$  under the ordinary pressure.

The laurene obtained by the distillation of camphoric acid is probably not an individual compound but a mixture of isomerides. Laurene as thus prepared was found to diminish in specific rotation ( $[\alpha]_D$ )

C <sub>5</sub> H <sub>11</sub> N.	1:1-Aminocyclopropylethane .....	830.2	831.5
C <sub>7</sub> H <sub>15</sub> N.	3-Amino-1-methylcyclohexane .....	1128.0	1129.9
C <sub>9</sub> H <sub>19</sub> N.	C <sub>7</sub> H <sub>13</sub> ·CHMe·NH <sub>2</sub> .....	1440.1	1442.6
C <sub>9</sub> H <sub>17</sub> NO.	C <sub>7</sub> H <sub>13</sub> ·CMe:OH .....	1375.3	1377.2

In some cases where only small quantities of isomeric cyclic compounds were available, the numbers differ to some extent, but, for such isomerides, the author is of opinion that the heats of combustion are either equal or very nearly so.

T. H. P.

**Piperylene and Tropilidene.** By JOHANNES THIELE (*Annalen*, 1901, 319, 226—230).—Piperylene, when oxidised with potassium permanganate solution, yields formic and acetic acids, a result which indicates that its constitution is that of  $\alpha\gamma$ -pentadiene,  $\text{CH}_2\text{:CH}\cdot\text{CH}\text{:CHMe}$ . If the hydrocarbon were divinylmethane, it should yield malonic acid. The hydrocarbon obtained by Armstrong and Miller (*Trans.*, 1886, 49, 74) from compressed oil gas is identical with piperylene. The piperylene tetrabromide ( $\alpha\beta\gamma\delta$ -tetrabromopentane) employed in characterising the hydrocarbon may crystallise either in prisms or leaflets melting at  $114\text{--}115^\circ$ . Divinylmethane should be the first product of the decomposition of dimethylpiperidine; the shifting of the double linkings may be due to the action of the trimethylamine; a similar action is observed in the preparation of *cycloheptadiene*, these examples illustrating the attraction of double linkings. Piperylene and tropilidene do not condense with benzophenone or ethyl oxalate in the presence of an alkali ethoxide, and the latter hydrocarbon does not react with diazobenzenesulphonic acid. This result is all the more surprising because tropilidene is undoubtedly a *cycloheptatriene*.

G. T. M.

**Thiosulphates of Aromatic Amines.** By A. WAHL (*Compt. rend.*, 1901, 133, 1215—1217).—On mixing solutions of sodium thiosulphate and aniline hydrochloride, *aniline thiosulphate*,  $(\text{NPhH}_2)_2\cdot\text{H}_2\text{S}_2\text{O}_3$ , is formed as a crystalline precipitate. Other primary amines of the benzene and naphthalene series yield similar thiosulphates; secondary and tertiary amines, on the other hand, do not give these salts, but react with the thiosulphate with formation of sulphur and sulphur dioxide. Such bases as dimethyl-*p*-phenylenediamine yield thiosulphates of the type  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{H}_2\text{S}_2\text{O}_3$ . When heated, these salts are decomposed, giving the base, sulphur dioxide, sulphur, and water.

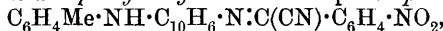
Nitrosodimethylaniline hydrochloride and sodium thiosulphate, when warmed together in aqueous solution, yield dimethyl-*p*-phenylenediamine sulphononic acid, representing 12—15 per cent. of the nitrosodimethylaniline used.

K. J. P. O.

**Derivatives of *p*-Tolyl- $\alpha$ -naphthylamine.** By ROBERT GNEHM and ED. A. RÜBEL (*J. pr. Chem.*, 1901, [ii], 64, 497—517).—*Acetyl-p-tolyl- $\alpha$ -naphthylamine*,  $\text{C}_{19}\text{H}_{17}\text{ON}$ , crystallises from ethyl acetate in small, white or pale flesh-coloured crystals, melts at  $124^\circ$ , and dissolves readily in organic solvents; it is not hydrolysed by dilute sulphuric acid at  $120\text{--}140^\circ$ , or by dilute alcoholic potassium hydroxide, but is hydrolysed by a 20 per cent. solution. The *benzoyl* derivative,  $\text{C}_{24}\text{H}_{19}\text{ON}$ , separates from ethyl acetate in yellow crystals, melts at  $140^\circ$ , and is hydrolysed much more readily than the acetyl derivative. The acetyl derivative is best sulphonated by leaving it with five times its weight of sulphuric monohydrate during two weeks; by this method, a *monosulphonic* acid is produced of which the *barium*

salt was analysed. *Barium p-tolyl- $\alpha$ -naphthylaminesulphonate* was prepared by hydrolysing the acetyl derivative with alcoholic potassium hydroxide, but was not obtained pure; the hydrolysis could not be carried out by boiling the diluted sulphonation mixture as in the case of acetyldiphenylaminesulphonic acid or by using hydrogen chloride or iodide.

*p-Tolyl- $\alpha$ -naphthylnitrosoamine*,  $C_{17}H_{14}ON_2$ , separates from alcohol or ether in golden-yellow crystals, and melts at  $102^\circ$ . Alcoholic hydrogen chloride converts it into the isomeric *p-tolyl-4-nitroso- $\alpha$ -naphthylamine* which crystallises from alcohol in blood-red needles and melts at  $161^\circ$ ; the *hydrochloride* forms brownish-black flakes with a bronze-like lustre, and melts at  $173^\circ$ . The hydrochloride condenses with  $\beta$ -naphthol to form an oxazime-dye, and is reduced by zinc dust to a diamine. The nitroso-base condenses with *p*-nitrobenzoyl cyanide to form *p-tolylamino- $\alpha$ -naphthyl-4-cyanazomethine-*p*-nitrophenyl*,



which separates from benzene in violet flakes with a bronze-like lustre, and from alcohol in brown, bronzy flakes, melts at  $218^\circ$ , and is hydrolysed by dilute acids to a diamine and nitrobenzoyl cyanide.

*Nitroacetyl-p-tolyl- $\alpha$ -naphthylamine*,  $C_{19}H_{16}O_3N_2$ , prepared by the action of nitric acid on *p*-tolyl- $\alpha$ -naphthylamine dissolved in acetic acid, crystallises from acetic acid and ethyl acetate, melts at  $240^\circ$ , and is not volatile with steam. When hydrolysed with alcoholic potassium hydroxide, it gives a yellow *nitrotolyl-naphthylamine*,  $C_{17}H_{14}O_2N_2$ , which melts at  $114^\circ$ ; an isomeric *nitro*-derivative, melting at  $188^\circ$ , was obtained by direct nitration of *p*-tolyl-naphthylamine. *Trinitro-p-tolyl-naphthylamine*,  $C_{17}H_{12}O_6N_4$ , melts at  $245^\circ$ , is insoluble in most solvents but dissolves in nitrobenzene and in aqueous alkalis.

*Monobromo-p-tolyl- $\alpha$ -naphthylamine*,  $C_{17}H_{14}NBr$ , melts at  $220^\circ$ , and is insoluble in all the ordinary solvents.

*Tetrabromo-p-tolyl- $\alpha$ -naphthylamine*,  $C_{17}H_{11}NBr_4$ , separates from benzene in well-formed crystals, melts at  $162^\circ$ , and is only slightly soluble in alcohol. By using a larger quantity of bromine, an isomeric *tetrabromo*-derivative was obtained, which crystallises in tablets and melts at  $212^\circ$ , together with a *hexabromo*-derivative,  $C_{17}H_9NBr_6$ , which crystallises in short, greenish-yellow prisms, melts at  $185^\circ$ , and is slowly decomposed by heating at  $115^\circ$ .

*p*-Tolyl- $\alpha$ -naphthylamine condenses with nitrosodimethyl-*m*-aminophenol to a quinoneimine-dye; the *colour-base*,  $C_{25}H_{21}ON_3$ , forms minute, brownish-red needles, and melts at  $199^\circ$ ; it can also be prepared from Meldola's blue and *p*-toluidine. The homologous *base*,  $C_{27}H_{25}ON_3$ , prepared by condensation with nitrosodiethyl-*m*-aminophenol, forms green needles, and melts at  $209.5^\circ$ .

A table is given showing the absorption spectra of this series of dyes.

T. M. L.

**Pseudophenols.** By KARL AUWERS (*Ber.*, 1901, **34**, 4256—4267).—A discussion of the results previously obtained (see Abstr., 1900, i, 96 and 161) and those detailed in the following three abstracts. The term pseudophenols is proposed for such as are insoluble in alkalis. With *o*- or *p*-cresol derivatives which contain one of the following sub-

stituents in the side chain—chlorine, bromine, iodine,  $-\text{NO}_2$ , or an acyl group—the compounds are insoluble in alkalis. When the substituent is  $-\text{OH}$ ,  $-\text{OR}$ ,  $-\text{CN}$ ,  $-\text{CO}_2\text{H}$ , or a positive radicle, the compounds are true phenols. These results, however, are subject to variation when there are substituents in the nucleus.

R. H. P.

**Nitro- and Thiocyno-pseudophenols and Cyanophenols.** By KARL AUWERS, C. SCHUMANN [and, in part, BROICHER] (*Ber.*, 1901, **34**, 4267—4282. See preceding abstract).—The compound previously described (Abstr., 1896, i, 421) as dibromo- $\psi$ -cumenol nitrite is a nitro-compound, and is best obtained by the action of silver nitrite on the acetate of dibromo- $\psi$ -cumenol bromide. Its *acetyl* derivative crystallises in felted needles, melts at  $155$ — $156^\circ$ , and when warmed with sodium methoxide yields dibromo- $p$ -hydroxy- $\psi$ -cumyl methyl ether. The free nitro-derivative of the pseudophenol is obtained in two forms by the action of sodium methoxide at the ordinary temperature on its acetate, namely, a stable melting at  $135^\circ$  (*loc. cit.*) and a labile one melting at  $110^\circ$ . Silver nitrate reacts with acetyldibromo- $\psi$ -cumenol bromide, forming *dibromo- $p$ -acetoxy- $\psi$ -cumyl nitrate*, which crystallises from methyl alcohol in slender, yellowish-white needles, and melts at  $137$ — $138^\circ$ . The bromide of the phenol does not react with silver nitrate in the same way, but yields either dibromo- $p$ -hydroxy- $\psi$ -cumyl alcohol or the corresponding *ether* which melts at  $254$ — $255^\circ$ . Analogous results were obtained by the action of silver nitrite and nitrate on the acetate of dibromo- $p$ -hydroxymesityl iodide; the *acetyl* derivative of the nitro-compound crystallises in slender needles melting at  $141^\circ$  and, when hydrolysed with a cold solution of sodium methoxide, yields the stable form of the *nitro*-compound which crystallises in needles melting at  $127$ — $128^\circ$ ; the *acetyl* derivative of the nitrate crystallises in slender needles melting at  $153$ — $154^\circ$ .

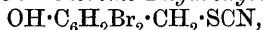
*Dibromo- $p$ -hydroxy- $\psi$ -cumyl thiocyanate*,  $\text{SCN} \cdot \text{CH}_2 \cdot \text{C} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \text{CH} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{OH}$ ,

obtained by the action of potassium thiocyanate on dibromo- $\psi$ -cumenol bromide, crystallises from light petroleum in needles, melts at  $112$ — $113^\circ$ , and is not dissolved by aqueous alkalis without decomposition; the *acetyl* derivative, which can only be obtained from the *acetyl* derivative of the bromide, crystallises in lustrous leaflets, melts at  $145$ — $146^\circ$ , and when hydrolysed with aqueous alkalis, yields the sulphide,  $\text{S}(\text{CH}_2 \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{OH})_2$  (Abstr., 1897, i, 35). The *diacetyl* derivative of the sulphide crystallises in needles and melts at  $232$ — $233^\circ$ . The *methyl ether* of the thiocyanate is obtained when the reaction between potassium thiocyanate and the bromide is carried out in absolute alcoholic solution; it crystallises in lustrous leaflets, melts at  $107$ — $108^\circ$ , and when treated with sodium methoxide yields the *dimethyl ether* of the disulphide,  $\text{S}_2(\text{CH}_2 \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{OMe})_2$ , which crystallises in felted needles melting at  $187$ — $188^\circ$ , and the *methyl ether* of the mercaptan,  $\text{OMe} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{SH}$ , which crystallises in needles melting at  $94$ — $95^\circ$ .

When the *acetyl* derivative of dibromo- $\psi$ -cumenol bromide is treated with potassium cyanide, a mixture of *dibromo- $p$ -acetoxy- $\psi$ -cumyl cyanide*,  $\text{OAc} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{CN}$ , and the *dibromo- $p$ -acetoxy- $\psi$ -cumyl ether* of dibromo- $p$ -hydroxy- $\psi$ -cumyl cyanide is obtained; the former is the more

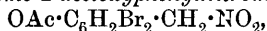
soluble in alcohol and crystallises in lustrous leaflets melting at 159—161°, the latter crystallises in slender, felted needles melting at 242—243°. *Dibromo-ψ-cumenol cyanide*,  $\text{OH} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{CN}$ , crystallises in slender, white needles melting at 171°, is soluble in alkalis and sodium carbonate, and when hydrolysed yields *dibromo-p-hydroxy-p-xylylacetic acid*, which crystallises in slender, white needles and melts at 216—218°. R. H. P.

**Pseudophenols.** By O. STEPHANI (*Ber.*, 1901, 34, 4283—4291. See preceding abstracts).—3 : 5-*Dibromo-2-hydroxybenzyl thiocyanate*,



obtained when dibromosaligenin dibromide is treated with potassium thiocyanate, crystallises in colourless clusters of needles melting at 111—112°, is insoluble in alkalis, and forms an *acetyl* derivative, which crystallises in thick, yellowish needles melting at 148—150°. 2 : 3 : 6-*Tribromo-3-hydroxybenzyl thiocyanate* crystallises in thick, yellowish needles melting at 121—122°, and is soluble in cold alkalis; its *acetyl* derivative crystallises in silky needles, and melts at 115°. 3 : 5-*Dibromo-4-hydroxybenzyl thiocyanate* crystallises in lustrous laminae melting at 108—109°, and is decomposed by alkalis.

The *acetyl* derivative of dibromosaligenin iodide crystallises from alcohol in needles, melts at 116—117°, and when treated with silver nitrite yields 3 : 5-*dibromo-2-acetoxyphenylnitromethane*,

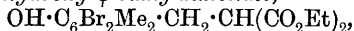


which crystallises in lustrous, slender needles, and melts at 132—133°; the corresponding *hydroxy*-compound crystallises in yellowish needles melting at 92—93°, and is decomposed by cold alkalis.

2 : 3 : 6-*Tribromo-3-hydroxybenzyl iodide* crystallises in yellowish needles melting at 119—120°. *Tribromo-3-hydroxyphenylnitromethane* crystallises in thick needles melting at 135—136°, and is soluble in alkalis.

In the course of this and previous researches of Auwers (*loc. cit.*), it was shown that of the dibromo-ψ-cumenol haloids the chloride is the least stable, and the author's attempt to prepare the fluoride failed.

*Ethyl dibromo-p-hydroxy-ψ-cumylmalonate*,



obtained by the action of the ψ-cumyl chloride on ethyl malonate in the presence of sodium, crystallises in plates melting at 92—93°; the *acid*, when heated at 173°, yields *dibromo-p-hydroxycumylacetic acid*, which crystallises in yellowish needles, melts at 170—171°, and is not altered when boiled with alkalis.

The *formate* and *amyl ether* of dibromo-p-hydroxy-ψ-cumyl alcohol were found to be similar in properties to analogous compounds previously described (*loc. cit.*); the *formate* crystallises in slender, white needles melting at 150—152°, and the *amyl ether* forms rhombic crystals melting at 84·5°. R. H. P.

**Nitroso-derivative of Methylphloroglucinol Dimethyl Ether.** By JACQUES POLLAK and M. SOLOMONICA (*Monatsh.*, 1901, 22, 1002—1010).—The constitution of the monomethyl ether of methylphloroglucinol having been shown by Konya (*Abstr.*, 1900, i, 545) to be  $[\text{OH} : \text{OH} : \text{Me} : \text{OMe} = 1 : 3 : 2 : 5]$ , that of the dimethyl ether must be  $[\text{OH} : \text{OMe} : \text{Me} : \text{OMe} = 1 : 3 : 2 : 5]$ .

The nitroso-derivative melts at  $160^{\circ}$ , and is reduced by stannous chloride to the corresponding amino-hydrochloride, which yields a triacetyl derivative melting at  $152\text{--}155^{\circ}$ . When heated with carbamide, the hydrochloride of the base is converted into 3:5-dimethoxy-2-methylcarbonyl-6-aminophenol,  $\text{C}_6\text{HMe}(\text{OMe})_2\text{<}\overset{\text{O}}{\text{N}}\text{>CO}$ , which crystallises from alcohol in delicate, greyish-white needles melting at  $188\text{--}189^{\circ}$ . On oxidation with ferric chloride, the base yields 3-hydroxy-5-methoxy-2-methylquinone; this crystallises in delicate red needles which melt at  $183\text{--}185^{\circ}$ . Etherification of the nitroso-derivative by sodium methoxide and methyl iodide leads to the formation of the methenyl compound,  $\text{C}_6\text{HMe}(\text{OMe})_2\text{<}\overset{\text{N}}{\text{O}}\text{>CH}$ , which crystallises in yellow leaves melting at  $72\text{--}74^{\circ}$ . These reactions show the *nitrosomethylphloroglucinol dimethyl ether* to have the nitroso-group in the *ortho*-position relatively to the hydroxyl.

G. Y.

**Chloromethyl Benzoate and Methylene Dibenzoate.** By MARCEL DESCUDÉ (*Compt. rend.*, 1901, 133, 1213—1214. Compare Abstr., 1901, i, 504, 644).—*Chloromethyl benzoate* (*loc. cit.*) is a colourless liquid which boils at  $210^{\circ}$  under 740 mm. pressure and at  $120\text{--}122^{\circ}$  under 12 mm. pressure, and has a sp. gr. 1.236 at  $20^{\circ}$ . Methylene dibenzoate is formed when chloromethyl benzoate is heated with dried potassium benzoate at  $150^{\circ}$ ; gaseous ammonia and the dibenzoate yield primarily benzamide and formaldehyde, which react together forming methylenedibenzamide (m. p.  $218^{\circ}$ ); at the same time, ammonium benzoate and hexamethylenetetramine are produced.

K. J. P. O.

**2-Chloro-3-naphthoic Acid.** By ERICH STROHBACH (*Ber.*, 1901, 34, 4158—4162).—*2-Chloro-3-naphthoyl chloride*,  $\text{C}_{10}\text{H}_6\text{Cl}\cdot\text{COCl}$ , prepared by heating 2-hydroxy-3-naphthoic acid and phosphorus pentachloride (3 mols.) at  $200\text{--}210^{\circ}$ , is an almost colourless, highly refractive oil boiling at  $248^{\circ}$  under 160 mm. pressure, which solidifies at  $56.5^{\circ}$  to a mass of lustrous needles. The acid chloride when warmed with water yields 2-chloro-3-naphthoic acid, this substance being obtained in snow-white crystals melting at  $216.5^{\circ}$  (compare Hosaeus, Abstr., 1893, i, 355).

*Ethyl 2-chloro-3-naphthoate*,  $\text{C}_{10}\text{H}_6\text{Cl}\cdot\text{CO}_2\text{Et}$ , produced by ethylating the acid with absolute alcohol and hydrogen chloride, crystallises from methyl alcohol in white leaflets; it melts at  $50^{\circ}$  and boils at  $218\text{--}222^{\circ}$  under 160 mm. pressure.

*2-Chloro-3-naphthamide*,  $\text{C}_{10}\text{H}_6\text{Cl}\cdot\text{CO}\cdot\text{NH}_2$ , formed by adding 2-chloro-3-naphthoyl chloride to concentrated ammonia solution, crystallises from glacial acetic acid in white needles melting at  $236\text{--}237^{\circ}$ .

*1-Chloro-2-naphthoyl chloride*,  $\text{C}_{10}\text{H}_6\text{Cl}\cdot\text{COCl}$ , prepared from 1-hydroxy-2-naphthoic acid and phosphorus pentachloride, crystallises from ether in aggregates of needles and melts indefinitely between  $48^{\circ}$  and  $60.5^{\circ}$ ; after solidifying, it melts at  $64\text{--}65^{\circ}$ . When distilled under 160 mm. pressure, the chloride boils at  $226^{\circ}$ ; it seems to contain traces of 1-chloro-2-naphthoyl trichloride,

G. T. M.

**Chlorobromo-3-hydroxybenzoic Acids and their Ethyl Esters.** By C. MARTINI (*Gazzetta*, 1901, 31, ii, 363—370).—*Ethyl 6-chloro-2-bromo-3-hydroxybenzoate*,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{ClBr} \cdot \text{CO}_2\text{Et}$ , obtained by the action of bromine on ethyl 6-chloro-3-hydroxybenzoate in acetic acid solution, crystallises from aqueous alcohol in slender, white, anhydrous needles melting at  $101\text{--}102^\circ$ . The corresponding *acid*, prepared either by hydrolysis of the ethyl ester or by the action of bromine on 6-chloro-3-hydroxybenzoic acid, separates from aqueous alcohol in small, white needles containing  $1\text{H}_2\text{O}$  and melting at  $194\text{--}195^\circ$ ; in aqueous solution, the acid gives a brownish-violet coloration with ferric chloride.

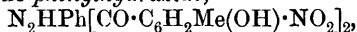
*Ethyl 2-chloro-6-bromo-3-hydroxybenzoate*, obtained by the action of bromine on ethyl 2-chloro-3-hydroxybenzoate, separates from its ethereal solution, on cooling in ice and salt, as a pasty mass which liquefies at the ordinary temperature ( $24^\circ$ ) and is only slightly volatile in a current of steam. The corresponding *acid*, prepared either by hydrolysing the ethyl ester or by brominating 2-chloro-3-hydroxybenzoic acid, separates from aqueous alcohol in small, dense crystals which contain  $1\text{H}_2\text{O}$  and melt with incipient decomposition at  $116\text{--}118^\circ$ ; with ferric chloride, it gives a violet coloration.

The two acids above described and the corresponding dichloro-acid [ $\text{CO}_2\text{H} : \text{Cl} : \text{Cl} : \text{OH} = 1 : 2 : 6 : 3$ ] all crystallise with  $1\text{H}_2\text{O}$ , and their ethyl esters crystallise in an anhydrous state, and are only hydrolysed with difficulty, even by concentrated potassium hydroxide solutions.

T. H. P.

**Some Derivatives of  $\beta$ -Cresotic Acid [2-Hydroxy-*m*-toluic Acid].** By MAX FORTNER (*Monatsh.*, 1901, 22, 939—954).—Nitration of 2-acetoxy-*m*-toluic acid and subsequent hydrolysis yields 5-nitro-2-hydroxy-*m*-toluic acid, which melts at  $199^\circ$ . Contrary to Einhorn's statement (*Abstr.*, 1900, i, 439), esterification of the nitro-acid takes place with hydrochloric acid and alcohol. The position of the nitro-group was determined by reduction of the ester to the amino-compound, which melted at  $106^\circ$ , and conversion of this, by Sandmeyer's reaction, into Thiele and Eichwede's *ethyl 5-bromo-2-hydroxy-*m*-toluate* [ $\text{Br} : \text{Me} : \text{OH} : \text{CO}_2\text{Et} = 5 : 3 : 2 : 1$ ], which melts at  $75^\circ$  (*Abstr.*, 1900, i, 501). Hydrolysis of the ester yielded the 5-bromo-acid melting at  $236^\circ$ . The position of the nitro-group is also shown by comparison of 5-amino-2-hydroxy-*m*-toluic acid with that of Nietzki and Ruppert. 5-Nitro-2-acetoxy-*m*-toluic acid separates from alcohol in yellowish crystals which melt at  $142^\circ$ .

5-Nitro-2-hydroxy-*m*-toluoyl chloride, prepared by the action of thionyl chloride, forms small, yellowish crystals which melt at  $86\text{--}88^\circ$  and have a characteristic aromatic odour. From the chloride were prepared the *amide*, which forms small, yellow crystals melting at  $231^\circ$ ; the *anilide*, yellowish needles which melt at  $208^\circ$ ; the *piperidide*, which separates from alcohol in small, yellowish, glistening needles melting at  $125^\circ$ ; the *phenylhydrazide*,



which separates slowly from alcohol or glacial acetic acid as a crystalline powder melting at  $255^\circ$ . The amide, anilide, and piperidide give



deep red colorations with ferric chloride. Attempts to brominate 5-nitro-2-hydroxy-*m*-toluic acid were unsuccessful.

The 5-bromo-acid may also be prepared almost quantitatively by bromination of 2-hydroxy-*m*-toluic acid in chloroform solution.

5-Bromo-2-acetoxy-*m*-toluic acid crystallises from alcohol in white needles which melt at 155°.

5-Bromo-2-hydroxy-*m*-toluoyl chloride, formed by the action of thionyl chloride, is easily soluble in benzene, from which it crystallises in rhombic plates melting at 80—85° and having a characteristic odour. From it were prepared the *ethyl ester*; the *amide*, which crystallises from alcohol in small leaves melting at 75—78°; the *anilide*, which melts at 125°; the *piperidide*, which melts at 82—84°. The amide, anilide, and piperidide give red to violet colorations with ferric chloride.

G. Y.

**Isomeric Dimethylcoumarones contained in Coal-tar.** By JOHANNES BOES (*Chem. Centr.*, 1901, ii, 1226; from *Pharm. Zeit.*, 46, 878).—Since the presence of *as-o*-xylenol and *as-p*-xylenol has been detected in the decomposition products of the coal-tar fraction boiling at 220—222° (Abstr., 1900, i, 31), this liquid, whilst consisting mainly of 4:6-dimethylcoumarone, must also contain a small quantity of 4:5-dimethylcoumarone, together, possibly, with traces of 3:6-dimethylcoumarone.

E. W. W.

**Organic Mercury Compounds.** By JOHANNES BOES (*Chem. Centr.*, 1901, ii, 1347—1348; from *Pharm. Zeit.*, 46, 915).—Coumarone and indene combine with mercuric sulphate to form the compounds  $C_8H_6O, 2HgSO_4, 2HgO, H_2O$  and  $C_9H_8, 2HgSO_4, 2HgO, H_2O$  respectively. These substances are best prepared by means of Denigès' mercuric sulphate solution (Abstr., 1895, i, 411) and are well suited for the quantitative separation of coumarone or indene from benzene solutions; they form yellow precipitates, are insoluble in water and the ordinary solvents, lose water at 100—110°, decompose above 200°, and when treated with hydrogen sulphide or warm hydrochloric acid regenerate the hydrocarbon.

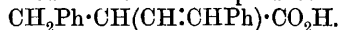
The compounds  $C_8H_6O, HgSO_4, 2HgO$  and  $C_9H_8, HgSO_4, 2HgO$ , prepared by shaking solutions of coumarone or indene respectively, diluted with pure methyl alcohol with the calculated quantity of a solution of mercuric sulphate, are also suitable, under certain conditions, for analytical purposes.

E. W. W.

**The Constitution of Unsaturated and Aromatic Compounds.** By JOHANNES THIELE (*Annalen*, 1901, 319, 129—143. Compare E. Erlenmeyer, jun., Abstr., 1901, i, 357, 373).—The formation of  $\alpha$ -benzyl- $\beta$ -benzylidenepropionic acid,  $CHPh:CH\cdot CH(CH_2Ph)\cdot CO_2H$ , from  $\alpha\beta$ -dibenzylidenepropionic acid,  $CHPh:CH\cdot C(CHPh)\cdot CO_2H$ , is no exception to the rule deduced from the author's theory that the hydrogen atoms should attach themselves to the ends of the system  $C:C:C:C$ , for the unreduced compound also contains the conjugate system  $C:C:C:O$  interlaced with the other chain in the following

manner,  $\text{C}:\text{C}:\underset{\text{C}}{\underset{|}{\text{C}}}:\text{C}:\text{O}$ . The hydrogen atoms may therefore be considered

to attach themselves to the ends of the system containing oxygen, forming the labile compound  $\text{CH}_2\text{Ph}\cdot\text{C}(\text{CH}:\text{CHPh})\cdot\text{C}(\text{OH})_2$ , which is immediately transformed into the stable product



This explanation applies equally well to the reduction of  $\gamma$ -phenyl- $\alpha$ -benzylidene- $\Delta^2$ -crotonolactone.

The existence of free triphenylmethyl has an important bearing on the theory of partial valency, and according to this hypothesis the fourth valency of the methyl carbon atom is almost entirely satisfied by the residual affinities of the carbon atoms of the aromatic nuclei.

The space formula for benzene adopted by Erlenmeyer, jun., consists of six regular tetrahedra arranged so that their bases lie in the same plane, forming a hexagon, their apical angles being situated on the same side of this plane. The theoretical conclusions deduced from this formula as to the behaviour of aromatic compounds are, however, invariably opposed to the facts of experiment.

According to this hypothesis, the carboxyl groups in terephthalic, isophthalic, and succinic acids have the same spacial relationship to each other, and the formation of anhydride should in each case take place with equal readiness. On this assumption, *p*-hydroxymethylbenzoic acid becomes an analogue of  $\gamma$ -hydroxybutyric acid and should readily furnish a lactone. These assumptions are directly opposed to the known behaviour of the compounds in question. Ethyleneglycol and catechol form monomolecular carbonates, but according to this hypothesis quinol is also an analogue of the glycol and should also accordingly yield a simple carbonate; resorcinol and quiniol, however, both form polymeric carbonates.

The central carbon atoms of a naphthalene molecule produced by the conjugation of two such benzene nuclei would be united by a double linking, and this portion should accordingly be the one most susceptible to the attack of substituting agents. This conclusion is manifestly incorrect and a similar fallacy is detected on applying the same line of argument to the anthracene molecule. The employment of a modification of this space formula in which the apical angles of the tetrahedra are placed alternately on opposite sides of the plane of the nucleus is attended with similar disadvantages. G. T. M.

**Unsaturated  $\gamma$ -Lactones.** By JOHANNES THIELE (*Annalen*, 1901, 319, 144—155. Compare following abstracts).—This theoretical communication contains a discussion of the four following memoirs.

The saturated  $\gamma$ -ketonic acids give rise to two series of crotonolactones,  $\text{CO} < \underset{\text{O}}{\underset{|}{\text{CR}}}:\text{CH}$  and  $\text{CO} < \underset{\text{O}}{\underset{|}{\text{CHR}}}:\text{CH}$ , these derivatives being indicated by the symbols  $\Delta^a$  and  $\Delta^b$  respectively. Sometimes a third isomeride is possible, as, for example, when the substituent X is a benzyl radicle; the isomerism of dihydrocornicularolactone and  $\alpha$ -phenyl- $\gamma$ -benzyl- $\Delta^a$ -crotonolactone is explained in this manner, these

isomerides containing extra- and intra-nuclear double linkings respectively.

The  $\Delta^{\alpha}$ -lactones, on oxidation with permanganate, yield dihydroxy-lactones,  $\text{CO} \begin{smallmatrix} \text{CX}(\text{OH}) \cdot \text{CH} \cdot \text{OH} \\ \text{O} \text{---} \text{CH} \cdot \text{R} \end{smallmatrix}$ , which in turn give rise to trihydroxy-acids,  $\text{OH} \cdot \text{CHR} \cdot \text{CH}(\text{OH}) \cdot \text{CX}(\text{OH}) \cdot \text{CO}_2\text{H}$ ; this reaction is not, however, perfectly general, for  $\beta\gamma$ -diphenyl- $\Delta^{\alpha}$ -crotonolactone is very slightly affected by the oxidising agent.

The  $\Delta^{\beta}$ -lactones, on oxidation, yield hydroxyketonic acids,  $\text{R} \cdot \text{CO} \cdot \text{CH}(\text{OH}) \cdot \text{CHX} \cdot \text{CO}_2\text{H}$ , the intermediate dihydroxylactones,  $\text{CO} \begin{smallmatrix} \text{CHX} \cdot \text{CH} \cdot \text{OH} \\ \text{O} \text{---} \text{CR} \cdot \text{OH} \end{smallmatrix}$ , being unstable.

The lactones of this series containing in the  $\alpha$ -position a methylene group between a carbonyl and an ethylene linking, readily condense with aldehydes in the presence of a weak base such as aniline; the corresponding  $\Delta^{\alpha}$ -derivatives do not react under these conditions. The  $\Delta^{\beta}$ -derivatives are usually labile and are converted into their stable  $\Delta^{\alpha}$ -isomerides by the action of acetic anhydride or a strong base such as ammonia, tropine, piperidine, or the aliphatic amines. Bases with a neutral reaction (aniline, pyridine, or their derivatives) do not bring about this transformation. The  $\Delta^{\alpha}$ -compound, however, is not invariably the stable modification, for in the case of the  $\gamma$ -phenylcrotonolactones, the isomeride of this series is readily transformed into its  $\Delta^{\beta}$ -isomeride. This characteristic action of the strong bases is analogous to that of alkaline reagents on the enolic forms of the esters of  $\beta$ -ketonic acids; in the latter case, a double linking shifts from the  $\cdot\text{C}:\text{C}\cdot$  to the  $:\text{C}:\text{O}$  group, whilst in the former, the rearrangement occurs between two  $\cdot\text{C}:\text{C}\cdot$  residues. The transformation of  $\Delta^{\beta}$ -lactone into its  $\Delta^{\alpha}$ -isomeride is reversed when the strong base reacts in the presence of an agent capable of condensing with the regenerated  $\Delta^{\beta}$ -lactone, the substance commonly employed being an aldehyde.

The reduction of ammoniacal silver nitrate by the  $\Delta^{\alpha}$ - and  $\Delta^{\beta}$ -crotonolactones varies in rapidity with the position of the double linking, and it also seems to depend on the presence of hydrogen in the  $\gamma$ -position of the lactone ring, for derivatives having the general

formula  $\text{CO} \begin{smallmatrix} \text{CH}:\text{C} \cdot \text{R} \\ \text{O} \text{---} \text{CXY} \end{smallmatrix}$  are not affected by this reagent.

Both series of unsaturated lactones develop an intense yellow coloration with alcoholic potassium hydroxide, which is supposed to be due to the formation of hydroxyfurfuranols,  $\text{OH} \cdot \text{C} \begin{smallmatrix} \text{CR} \cdot \text{CR} \\ \text{O} \text{---} \text{C} \cdot \text{R} \end{smallmatrix}$ , substances which could be produced by a simple transformation from both  $\Delta^{\alpha}$ - and  $\Delta^{\beta}$ -derivatives. Lactones such as phenylbenzylidenebutylolactone and dihydrocornicularolactone, which contain a double linking outside the lactone ring, do not exhibit this property.

The following communications furnish experimental evidence in favour of the hypothesis that the two series of crotonolactones are structurally dissimilar and not stereoisomerides as suggested by Erlenmeyer, jun. (compare Abstr., 1901, i, 357, 373). G. T. M.

**The Lactones of Desylacetic Acid.** By JOHANNES THIELE and FRITZ STRAUS (*Annalen*, 1901, 319, 155—180. Compare Abstr., 1899, i, 612; Klingemann, Abstr., 1892, 1002, and Erlenmeyer and Lux,

Abstr., 1898, i, 668).— $\beta\gamma$ -Diphenyl- $\Delta^{\beta}$ -crotonolactone,  $\text{CO} \begin{smallmatrix} \text{CH}_2 \cdot \text{CPh} \\ \text{O} - \text{CPh} \end{smallmatrix}$ , readily reduces ammoniacal silver nitrate and potassium permanganate solutions, and is converted into its stable  $\Delta^{\alpha}$ -isomeride,  $\text{CO} \begin{smallmatrix} \text{CH} \cdot \text{CPh} \\ \text{O} - \text{CHPh} \end{smallmatrix}$ , when boiled with alcohol containing traces of a base or salt having an alkaline reaction; the catalysts employed are potassium carbonate or hydroxide, sodium acetate, ammonia, piperidine, or an aliphatic amine. The aromatic bases do not promote this transformation.

$\beta\gamma$ -Diphenyl- $\alpha$ -benzylidene- $\Delta^{\beta}$ -crotonolactone,  $\text{CHPh} \cdot \text{C} \begin{smallmatrix} \text{CPh} \cdot \text{CPh} \\ \text{CO} - \text{O} \end{smallmatrix}$ ,

produced by boiling together its generators in alcohol containing a trace of aniline, crystallises from this solvent in yellow needles melting at 141—142°; it is also obtained by heating the stable lactone with benzaldehyde containing a few drops of piperidine. The latter mode of formation indicates that the transformation of the labile lactone with the  $\Delta^{\alpha}$ -isomeride by the aid of piperidine is a reversible process.

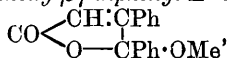
*Desylcinnamic acid*,  $\text{COPh} \cdot \text{CHPh} \cdot \text{C}(\text{CHPh}) \cdot \text{CO}_2\text{H}$ , results from the action of a methyl alcoholic solution of potassium hydroxide on the preceding compound; it separates from benzene as a white, crystalline powder, and melts at 187—188°. The *methyl ester*, obtained from the silver salt and methyl iodide, crystallises from alcohol in lustrous, white needles and melts at 113.5°. The acid and its ester develop an intense yellow coloration with alcoholic potassium hydroxide, but it is destroyed by the addition of water. When treated with acetic anhydride and a trace of sulphuric acid, the acid yields  $\gamma$ -*acetoxy- $\beta\gamma$ -diphenyl- $\alpha$ -benzylidenebutylolactone*,  $\text{OAc} \cdot \text{CPh} \begin{smallmatrix} \text{CHPh} \cdot \text{C} \cdot \text{CHPh} \\ \text{O} - \text{CO} \end{smallmatrix}$ , a substance crystallising from alcohol in colourless, iridescent plates melting at 128—128.5°.

$\alpha$ -Bromo- $\beta\gamma$ -diphenyl- $\Delta^{\alpha}$ -crotonolactone,  $\text{CO} \begin{smallmatrix} \text{CBr} \cdot \text{CPh} \\ \text{O} - \text{CHPh} \end{smallmatrix}$ , prepared by treating thin layers of the powdered  $\Delta^{\alpha}$ -lactone with bromine vapour in the presence of light, crystallises from alcohol or carbon disulphide in colourless needles and melts at 118—119°; it is somewhat insoluble in the ordinary organic solvents, reduces ammoniacal silver nitrate, regenerates the  $\Delta^{\alpha}$ -lactone when treated with alcohol and a zinc-copper couple, but is not attacked by zinc dust and cold acetic acid.

$\beta\gamma$ -Dibromo- $\beta\gamma$ -diphenylbutylolactone,  $\text{CO} \begin{smallmatrix} \text{CH}_2 \cdot \text{CPhBr} \\ \text{O} - \text{CPhBr} \end{smallmatrix}$ , produced by adding the  $\Delta^{\beta}$ -lactone dissolved in carbon disulphide to a cooled solution of bromine in the same solvent, separates as a white, crystalline powder which decomposes at 64° evolving hydrogen bromide and yielding  $\gamma$ -bromo- $\beta\gamma$ -diphenyl- $\Delta^{\alpha}$ -crotonolactone,  $\text{CO} \begin{smallmatrix} \text{CH} \cdot \text{CPh} \\ \text{O} - \text{CPhBr} \end{smallmatrix}$ , a sub-

stance crystallising from light petroleum in well-defined, brownish prisms, melting at 107—108° and decomposing at 130°.

The mono-bromolactone yields the labile  $\Delta^{\alpha}$ -lactone on reduction with zinc dust and glacial acetic acid, and when warmed with methyl alcohol gives rise to  $\gamma$ -methoxy- $\beta\gamma$ -diphenyl- $\Delta^{\alpha}$ -crotonolactone,



which separates from this solvent in colourless crystals melting at 102.5°.

$\gamma$ -Acetoxy- $\beta\gamma$ -diphenyl- $\Delta^{\alpha}$ -crotonolactone,  $\text{CO} \begin{array}{l} \diagup \text{CH} \cdot \text{CPh} \\ \diagdown \text{O} - \text{CPh} \cdot \text{OAc} \end{array}$ , produced

by shaking an ethereal solution of the bromo-lactone with silver acetate, crystallises from methyl alcohol or benzene, and melts at 116°.

Desyleneacetic acid,  $\text{CPh} \cdot \text{CPh} \cdot \text{CH} \cdot \text{CO}_2\text{H}$ , prepared from  $\beta\gamma$ -dibromo- $\beta\gamma$ -diphenylbutyrolactone by the action of a cold alcoholic solution of potassium hydroxide, is also obtained by oxidising the  $\Delta^{\beta}$ -lactone with a potassium permanganate solution containing magnesium sulphate, and is produced in small quantities along with desylacetic acid when the dibromide is converted into  $\gamma$ -bromo- $\beta\gamma$ -diphenyl- $\Delta^{\alpha}$ -crotonolactone by the action of heat; it crystallises from benzene and melts at 139°; the solidified product, however, has a melting point of 167°. The two modifications, when mixed together, melt at 167°. These two modifications of the acid seem to have a transformation temperature which is below the melting point of the substance melting at 139°; this form is distinguished as the  $\alpha$ -, and the other as the  $\beta$ -compound. The  $\alpha$ -acid, when heated at 130—135°, changes into the  $\beta$ -compound, whilst this substance, when dissolved in ammonia and precipitated by acid, regenerates the acid of lower melting point. The silver salts obtained from the two modifications yield the same methyl ester on treatment with methyl iodide; this derivative forms lustrous needles melting at 89°, and is isomeric with  $\gamma$ -methoxy- $\beta\gamma$ -diphenyl- $\Delta^{\alpha}$ -crotonolactone. Desyleneacetic acid may also be obtained from  $\beta$ -bromo- $\beta\gamma$ -diphenyl- $\Delta^{\alpha}$ -crotonolactone or  $\gamma$ -methoxy- $\beta\gamma$ -diphenyl- $\Delta^{\alpha}$ -crotonolactone by the action of alcoholic solutions of potassium hydroxide; it is identical with the product from desylenemalonic acid (Japp, Trans., 1895, 67, 138; 1897, 71, 133).

Ethyl desylenemalonate,  $\text{CPh} \cdot \text{CPh} \cdot \text{C}(\text{CO}_2\text{Et})_2$ , when crystallised from alcohol, melts at 70—71°.

Deoxybenzoin is readily prepared by treating chlorobenzil with granulated zinc and alcoholic hydrochloric acid. G. T. M.

**The Lactones of Angelic Acid.** By JOHANNES THIELE, ROBERT TISCHBEIN and EMIL LOSSOW (*Annalen*, 1901, 319, 180—195).— $\Delta^{\beta}(\alpha)$ -Angelicalactone, prepared from lævulic acid by Bredt's method (Abstr., 1890, 863), yields  $\alpha$ -anisylidene- $\Delta^{\beta}$ -angelicalactone,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{C} \begin{array}{l} \diagup \text{CH} \cdot \text{CMe} \\ \diagdown \text{CO} - \text{O} \end{array}$ , when condensed with anisaldehyde, and  $\alpha$ -benzylidenelævulic acid,  $\text{COMe} \cdot \text{CH}_2 \cdot \text{C}(\text{CHPh}) \cdot \text{CO}_2\text{H}$ ; when treated with benzaldehyde; the former product crystallises from methyl alcohol in yellow needles melting at 98.5—99°, and the latter in white

needles melting at  $121^{\circ}$  (compare Erdmann, Abstr., 1900, 375, 1129). The condensations are carried out in the presence of a trace of piperidine; when the reaction with benzaldehyde is performed in a methyl alcohol solution of potassium hydroxide, a *dibenzylidenelævulic acid* is obtained which forms colourless needles melting at  $177$ — $178^{\circ}$ , and differs from Erdmann's  $\beta\delta$ -dibenzylidenelævulic acid (*loc. cit.*)

*Benzylidenemalic acid*,  $\text{HO}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{C}(\text{CHPh})\cdot\text{CO}_2\text{H}$ , and iodoform are obtained on treating  $\alpha$ -benzylidenelævulic acid with iodine and sodium hydroxide; the acid separates from water in white crusts

melting at  $173^{\circ}$  and yields the *anhydride*,  $\text{CHPh}\cdot\text{C}\begin{array}{c} \text{---CO} \\ \text{---CO}_2\text{Me}\cdot\text{CH}\cdot\text{CO} \end{array} \text{O}$ , of

$\beta$ -acetyl- $\alpha$ -benzylidenemalic acid, a substance crystallising from benzene and light petroleum in white needles melting at  $116.5$ — $117^{\circ}$ .  $\alpha$ -*Anisylidenelævulic acid*,  $\text{CH}_2\text{Ac}\cdot\text{C}(\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})\cdot\text{CO}_2\text{H}$ , obtained from the corresponding lactone by treating it with crystallised sodium carbonate in dilute alcoholic solution and acidifying the product, crystallises from toluene in needles melting at  $119$ — $119.5^{\circ}$ ; the lactone is regenerated by the action of acetic anhydride and a trace of sulphuric acid.

*Anisylidenemalic acid*,  $\text{CO}_2\text{H}\cdot\text{CH}(\text{OH})\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , produced together with iodoform by the action of iodine and sodium hydroxide on the preceding acid, forms white needles sintering at  $165^{\circ}$  and decomposing at  $177^{\circ}$ .

The formation of condensation products from  $\alpha$ -angelicalactone and the aldehydes shows that it has a constitution corresponding with the formula  $\text{CO} < \begin{array}{c} \text{CH}_2\cdot\text{CH} \\ \text{O} \text{---} \text{CMe} \end{array}$ . It is partially transformed into the  $\beta$ - or

$\Delta^{\alpha}$ -angelicalactone,  $\text{CO} < \begin{array}{c} \text{CH}\cdot\text{CH}_2 \\ \text{O} \text{---} \text{CMe} \end{array}$ , by heating with diethylaniline hydrobromide, or triethylamine; the converse transformation occurs to a limited extent on warming the purified  $\Delta^{\alpha}$ -isomeride with the latter reagent.  $\Delta^{\alpha}$ -Angelicalactone does not combine with anisaldehyde, but when oxidised with potassium permanganate solution containing mag-

nesium sulphate yields *dihydroxyvalerolactone*,  $\text{CO} < \begin{array}{c} \text{CH}(\text{OH})\cdot\text{CH}\cdot\text{OH} \\ \text{O} \text{---} \text{CHMe} \end{array}$ ,

which crystallises from water, alcohol, or ethyl acetate in colourless needles melting at  $100^{\circ}$ ; its *diacetyl* derivative, obtained by the action of acetyl chloride, crystallises from alcohol in colourless needles melting at  $94$ — $95^{\circ}$ . Barium trihydroxyvalerate, produced by dissolving the lactone in barium hydroxide solution, is an uncrystallisable salt; the corresponding acid is unstable and regenerates the lactone. Alkaline solutions of the lactone do not reduce ammoniacal silver nitrate. The stability of the dihydroxylactone under these conditions is evidence in favour of its formula and also of that proposed for  $\Delta^{\alpha}$ -angelicalactone. The dihydroxylactones derived from  $\Delta^{\beta}$ -angelicalactone and

its  $\Delta^{\gamma}$ -isomeride,  $\text{CO} < \begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ \text{O} \text{---} \text{C}\cdot\text{CH}_2 \end{array}$ , should have the formulæ,  $\text{CO} < \begin{array}{c} \text{CH}_2\cdot\text{CH}\cdot\text{OH} \\ \text{O} \text{---} \text{CMe}\cdot\text{OH} \end{array}$  and  $\text{CO} < \begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ \text{O} \text{---} \text{C}(\text{OH})\cdot\text{CH}_2 \end{array} \cdot\text{OH}$  respectively, and

the corresponding acids of the salts produced from these by the action of alkali hydroxides would be the hydroxylævulic acids,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{COMe}$  and  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$ , both of which, being  $\alpha$ -hydroxyketones, ought to reduce the silver solution.

G. T. M.

[Phenyl  $\Delta^\alpha$ -Crotonolactone]. The Unsaturated  $\Delta^\alpha$ -Lactone of Benzoylpropionic Acid. By JOHANNES THIELE and N. SALZBERGER (*Annalen*, 1901, 319, 196—211).— $\beta$ -Bromo- $\alpha$ -acetoxy- $\gamma$ -phenylbutyrolactone,  $\text{CO} \begin{smallmatrix} \text{CH}(\text{OAc})\cdot\text{CHBr} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{CHPh} \end{smallmatrix}$ , prepared from the corresponding

hydroxylactone by the action of acetic anhydride, crystallises from alcohol in colourless, vitreous, monoclinic prisms, and melts at  $64.5^\circ$ .

Phenyl  $\Delta^\alpha$ -crotonolactone,  $\text{CO} \begin{smallmatrix} \text{CH}\cdot\text{CH} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{CHPh} \end{smallmatrix}$ , obtained from the preceding compound by the action of a copper-zinc couple suspended in cold water, is a yellowish-red oil which solidifies in a freezing mixture, and when warmed with acetic anhydride or an alcoholic solution of piperidine or even on distillation at  $140^\circ$  under 30 mm. pressure, changes into its solid isomeride phenyl- $\Delta^\beta$ -crotonolactone,  $\text{CO} \begin{smallmatrix} \text{CH}_2\cdot\text{CH} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{CPh} \end{smallmatrix}$ ,

melting at  $91^\circ$  (compare Fittig, Abstr., 1898, i, 196, and Kugel, *ibid.*, 198). A slow transformation occurs even when the labile  $\Delta^\alpha$ -compound is kept in the dark but the change is not complete even at the end of twelve months. The  $\Delta^\alpha$ -lactone, when hydrolysed either with mineral acids or alkali hydroxides, yields  $\beta$ -benzoylpropionic acid (m. p.  $115$ — $116^\circ$ ), and on oxidation with potassium permanganate in the presence of magnesium sulphate gives rise to  $\alpha\beta$ -dihydroxy- $\gamma$ -phenylbutyrolactone (Fischer and Stewart, Abstr., 1892, 1447), whilst the  $\Delta^\beta$ -isomeride furnishes the red compound obtained by Kugel (*loc. cit.*) by the action of ferric chloride.

$\alpha$ -Acetoxy- $\gamma$ -phenylcrotonic acid,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}(\text{OAc})\cdot\text{CO}_2\text{H}$ , a by-product in the preparation of phenyl  $\Delta^\alpha$ -crotonolactone, crystallises from water in colourless needles containing  $1\text{H}_2\text{O}$ , and melting at  $78$ — $79^\circ$ ; the anhydrous acid, obtained by drying the monohydrate over concentrated sulphuric acid, melts at  $90$ — $91^\circ$ , and rapidly regains its water of crystallisation on exposure to the atmosphere. The acid, when treated with a chloroform solution of bromine, yields the dibromide (m. p.  $206^\circ$ ; compare Abstr., 1899, i, 611), and on boiling with hydrochloric acid gives rise to  $\beta$ -benzoylpropionic acid; it decomposes into acetic acid and phenyl  $\Delta^\beta$ -crotonolactone on distillation in a vacuum, a small amount of the  $\Delta^\alpha$ -isomeride being obtained by rapid heating.

$\alpha$ -Chloro- $\beta\gamma$ -dibromo- $\gamma$ -phenylbutyronitrile,  $\text{CHPhBr}\cdot\text{CHBr}\cdot\text{CHCl}\cdot\text{CN}$ , produced by treating the dibromide of cinnamaldehyde cyanohydrin with phosphorus pentachloride, crystallises from alcohol in colourless needles which melt somewhat indefinitely at  $110$ — $120^\circ$ ; when mixed with zinc dust and glacial acetic acid, it yields phenylcrotononitrile,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CN}$  or  $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CH}\cdot\text{CN}$ , a substance crystallising from light petroleum in leaflets melting at  $59$ — $60^\circ$  and rapidly reducing ammoniacal silver nitrate.

*βγ-Dibromo-α-acetoxy-γ-phenylbutyronitrile*,  
 $\text{CHPhBr} \cdot \text{CHBr} \cdot \text{CH}(\text{OAc}) \cdot \text{CN}$ ,

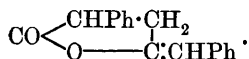
formed from the corresponding hydroxy-compound by the action of acetic anhydride, crystallises from alcohol in colourless, four-sided plates and melts at 166—167°. G. T. M.

**Unsaturated Lactones of Dihydrocornicularic Acid.** By JOHANNES THIELE and FRITZ STRAUS (*Annalen*, 1901, 319, 211—225. Compare Abstr., 1899, i, 612, 614).—*βγ-Dibromo-αδ-diphenylvaleric acid*,  $\text{CH}_2\text{Ph} \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{CHPh} \cdot \text{CO}_2\text{H}$ , prepared from *αδ*-diphenyl- $\Delta^\beta$ -pentoic acid and an acetic acid solution of bromine, crystallises from carbon disulphide in white needles melting at 172°. The bromine atoms are readily removed by the action of zinc dust and glacial acetic acid.

*α-Phenyl-γ-benzyl-Δ<sup>α</sup>-crotonolactone*,  $\text{CO} \begin{array}{l} \text{CPh} \cdot \text{CH} \\ \text{O} \text{---} \text{CH} \cdot \text{CH}_2\text{Ph} \end{array}$ , obtained

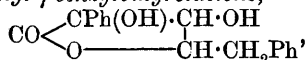
by treating the preceding dibromide with cold dilute sodium hydroxide solution, crystallises from methyl alcohol in thick, white needles and melts at 91°. The lactone is not affected by hydrogen bromide dissolved in glacial acetic acid, alcoholic hydrochloric acid, or hot acetic anhydride; it immediately reduces ammoniacal silver nitrate, and develops a deep yellow coloration with alcoholic potassium hydroxide solution. Dihydrocornicularic acid is obtained by boiling the lactone either with potassium hydroxide in methyl alcohol, or with a dilute alcoholic solution of sodium carbonate; by the former process, a small amount of a dimeric phenylbenzylcrotonolactone is simultaneously produced; this compound crystallises in lustrous prisms melting at 193°.

Dihydrocornicularic acid is identical with the product obtained by Spiegel (Abstr., 1882, 1077). This substance, according to the authors' experiments, is reconverted into the original lactone when heated at 200°; Spiegel, on the contrary, obtained a different compound, dihydrocornicularolactone, to which he ascribed the formula



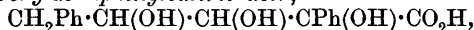
The polymeric lactone also yields the acid on treatment with potassium hydroxide in methyl alcohol; it reduces ammoniacal silver nitrate, but is not oxidised by alkaline solutions of permanganate.

*αβ-Dihydroxy-α-phenyl-γ-benzylbutyrolactone*,



results from the oxidation of *α*-phenyl-*γ*-benzyl- $\Delta^\alpha$ -crotonolactone with potassium permanganate solution; it crystallises from chloroform in white needles and melts at 138°; its *diacetyl* derivative forms lustrous prisms and melts at 137°.

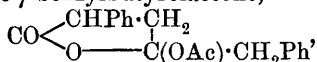
*αβγ-Trihydroxy-αδ-diphenylvaleric acid*,



obtained in the form of its *barium* salt by hydrolysing the dihydroxylactone with barium hydroxide solution, is unstable and regenerates the lactone. The *silver* salt,  $\text{C}_{17}\text{H}_{17}\text{O}_5\text{Ag}$ , is a hygroscopic, amorphous, white precipitate.



$\gamma$ -Acetoxy- $\alpha$ -phenyl- $\gamma$ -benzylbutyrolactone,



produced from dihydrocornicularic acid by the action of acetic anhydride and sulphuric acid, melts at 105–106° and not at 98–99° as recorded by Spiegel. Dihydrocornicularolactone is formed during the crystallisation of the acetoxy-compound and is obtained in larger quantities by treating the acid with half its weight of acetic anhydride and a trace of an acid; it is converted into its isomeride  $\alpha$ -phenyl- $\gamma$ -benzyl- $\Delta^{\alpha}$ -crotonolactone by heating with a glacial acetic acid solution of hydrogen bromide, but this transformation is not affected by acetic anhydride.

A lactone,  $\text{C}_{17}\text{H}_{14}\text{O}_2$ , isomeric with dihydrocornicularolactone, is produced together with this lactone and its acetyl derivative by heating dihydrocornicularic acid with acetic anhydride, traces of phenylbenzyl- $\Delta^{\alpha}$ -crotonolactone are also obtained; it crystallises from alcohol in highly refractive leaflets and melts at 128.5°. The new lactone is probably a stereoisomeride of dihydrocornicularolactone, and resembles the latter in reducing ammoniacal silver nitrate rapidly, but not instantaneously, and in developing a yellow coloration with alcoholic potassium hydroxide; it regenerates dihydrocornicularic acid by alkaline hydrolysis.

G. T. M.

**Naphthaldehydic Acid.** By JOSEF ZINK (*Monatsh.*, 1901, 22, 986–990).—When naphthaldehydic acid is formed by fusing acenaphthenequinone with potash, it is accompanied by naphthalic acid, the amount of the latter increasing with the duration of the fusion. Naphthalic acid is also formed on boiling naphthaldehydic acid with alkalis. The formation of a hydroxy-acid or lactone corresponding with phthalide could not be detected. Potassium cyanate in absolute alcohol has the same action as aqueous alkalis.

*Methyl naphthaldehydate* melts at 105° (compare Wegscheider, *Monatsh.*, 1882, 348).

G. Y.

**New Glyceride: Glyceryl Phthalate.** By WATSON SMITH (*J. Soc. Chem. Ind.*, 1901, 20, 1075–1076).—When glycerol and phthalic anhydride are heated for a long time nearly to boiling, either alone or with zinc chloride, the product is a solid mass resembling glass slag in appearance, which is most probably *diglyceryl triphthalate*. It is practically insoluble in all solvents, with the exception of acetone, in which it dissolves to a slight extent. On hydrolysis with sodium hydroxide, it yields glycerol and phthalic acid; with sulphuric acid, it gives sulphonated products, and it is nitrated by a mixture of concentrated nitric and sulphuric acids.

H. R. LE S.

**Derivatives of Nitrophthalic Acid.** By HEINRICH SEIDEL (*Ber.*, 1901, 34, 4351–4353. Compare Onnertz, this vol., i, 95).— $\beta$ -Nitrophthalic acid yields  *$\beta$ -nitrophthalimide* when heated in gaseous ammonia; this crystallises in yellowish leaflets melting at 202°;  $\alpha$ -nitrophthalimide forms yellowish needles melting at 216°. From the  $\alpha$ -imide, by means of Hofmann's reaction, 6-nitro-2-aminobenzoic acid,

$\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{CO}_2\text{H}$ , is obtained as an ochre-yellow, crystalline powder melting at  $184^\circ$ ; the acid readily loses carbon dioxide, with formation of *m*-nitroaniline. The  $\beta$ -imide yields two isomerides, 4-nitro-2-aminobenzoic acid melting at  $264^\circ$  and 5-nitro-2-aminobenzoic acid melting at  $280^\circ$ . From the former, 4-nitrosalicylic acid (m. p.  $235^\circ$ ) and 4-aminosalicylic acid (m. p.  $220^\circ$  with decomposition) can be obtained. The two nitrophthalic acids are reduced by sodium sulphide to *aminophthalic acids*; the  $\alpha$ -amino-acid is a yellow powder melting at  $226^\circ$ , whilst the  $\beta$ -amino-acid crystallises in needles, which lose their crystalline form on drying and melt at  $280^\circ$ . K. J. P. O.

$\alpha$ -Phenylglutaric Acid and  $\gamma\delta$ -Diphenylallylacetic Acid [ $\gamma\delta$ -Diphenyl- $\gamma$ -pentenoic Acid]. By FRITZ FICHTER and OTTO MERCKENS (*Ber.*, 1901, 34, 4174—4178).—Ethyl  $\gamma$ -acetyl- $\alpha$ -phenylglutarate,  $\text{CO}_2\text{Et} \cdot \text{CHAc} \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{CO}_2\text{Et}$ , obtained by condensing ethyl chlorohydratropate (Spiegel, *Abstr.*, 1881, 277) with ethyl sodioacetoacetate, boils at  $189^\circ$  under 11 mm. pressure, and, on hydrolysis with 25 per cent. alcoholic potassium hydroxide, yields  $\alpha$ -phenylglutaric acid; the latter is also obtained by heating with hydrochloric acid ethyl  $\alpha$ -phenylpropane- $\alpha\alpha$ -tricarboxylate, which is formed by condensing ethyl  $\beta$ -iodopropionate with ethyl phenylmalonate, and boils at  $219$ — $221^\circ$  under 13 mm. pressure.

$\alpha$ -Phenylglutaric acid is best purified in the form of its calcium salt, which crystallises in white, microscopic needles with  $4\text{H}_2\text{O}$ ; the barium salt, with  $2\text{H}_2\text{O}$ , is ill-defined, the zinc salt, with  $7\text{H}_2\text{O}$ , forms sheaves of needles, and the silver salt is anhydrous. The pure acid separates from benzene or light petroleum in small crystals, melts at  $82$ — $83^\circ$ , and partially changes in dry air into the anhydride; the latter is obtained quantitatively on distilling the acid under reduced pressure and crystallises from ether in beautiful, small needles, melts at  $95^\circ$ , and boils at  $218$ — $230^\circ$  under 13 mm. pressure. On boiling the anhydride with water, a hydrated form (with  $1\text{H}_2\text{O}$ ) of  $\alpha$ -phenylglutaric acid is obtained in large, colourless needles.

When dry sodium  $\alpha$ -phenylglutarate is heated with benzaldehyde (1 mol.) and acetic anhydride for 50 hours at  $155^\circ$ , considerable quantities of  $\gamma\delta$ -diphenylallylacetic acid [ $\gamma\delta$ -diphenyl- $\gamma$ -pentenoic acid],  $\text{CHPh} \cdot \text{CPh} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , are formed; it is best isolated in the form of the sparingly soluble, amorphous calcium salt (with  $1\frac{1}{2}$ — $2\text{H}_2\text{O}$ ); the barium salt contains  $2\text{H}_2\text{O}$ . The pure acid crystallises from a mixture of ether and light petroleum in colourless needles, melts at  $106^\circ$ , and when treated with hydrogen bromide in glacial acetic acid at the ordinary temperature, yields an oil which is readily transformed into  $\gamma\delta$ -diphenylvalerolactone; this separates from ether in beautiful crystals and melts at  $59$ — $60^\circ$ . W. A. D.

Anhydrous Methyl Gallate. By GIROLAMO MAZZARA (*Gazzetta*, 1901, 31, ii, 347—356).—Whilst ethyl gallate crystallises with  $2\frac{1}{2}\text{H}_2\text{O}$ , it has been stated by Biétrex (*Abstr.*, 1893, i, 343) that the methyl compound contains  $3\text{H}_2\text{O}$ . In this case, then, there appears to be no analogy similar to that existing between the methyl and ethyl esters of the dihalogenated gallic acids, which all crystallise with

$1\frac{1}{2}\text{H}_2\text{O}$ . The author finds, however, that when the anhydrous methyl gallate described by Will (Abstr., 1888, 1059) is crystallised several times from water it contains  $1\frac{1}{4}\text{H}_2\text{O}$ ; this hydrate, which he assumes to be a compound of the anhydrous ester with the hydrate containing  $2\frac{1}{2}\text{H}_2\text{O}$ , readily reverts to the anhydrous form. Ethyl gallate melts at  $158^\circ$  if crystallised from benzene, or at  $155^\circ$  if it is crystallised from water (with  $2\frac{1}{4}\text{H}_2\text{O}$ ) and dehydrated. T. H. P.

**Action of Bromine on Methyl and Ethyl Gallates and on their Chloro-derivatives.** By P. GUARNIERI (*Gazzetta*, 1901, 31, ii, 356—363).—Ethyl dibromogallate crystallises with  $1\frac{1}{2}\text{H}_2\text{O}$  and melts at  $137^\circ$ . Methyl dibromogallate, which Biétrex (Abstr., 1893, i, 343) described as crystallising with  $1\text{H}_2\text{O}$  and melting at  $139^\circ$ , is found by the author to contain  $1\frac{1}{2}\text{H}_2\text{O}$  and to melt at  $169^\circ$ .

*Ethyl Chlorobromogallate*,  $\text{C}_6\text{H}_5\text{BrCl}(\text{OH})_3\cdot\text{CO}_2\text{Et}$  [ $\text{Cl}:\text{Br}:(\text{OH})_3 = 2:6:3:4:5$ ], prepared by the action of bromine on ethyl chlorogallate in acetic acid solution, separates from water in leaflets containing  $1\frac{1}{2}\text{H}_2\text{O}$ , and melting, after dehydration, at  $134$ — $135^\circ$ . *Methyl chlorobromogallate* crystallises from water in yellow leaflets containing  $1\frac{1}{2}\text{H}_2\text{O}$ , and melting after dehydration at  $162$ — $163^\circ$ .

All the halogenated methyl and ethyl esters of gallic acid melt at lower temperatures than the esters from which they are derived; the disubstituted derivatives of methyl and ethyl gallates crystallise with  $1\frac{1}{2}\text{H}_2\text{O}$ , whilst the monohaloid compounds contain only  $1\text{H}_2\text{O}$ . The methyl esters in all cases melt at higher temperatures than the corresponding ethyl compounds. T. H. P.

**Interaction of Tannin and Tartar Emetic.** By NICOLAI N. LJUBAVIN (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 680—684).—The author has studied the action taking place when solutions of tannin and tartar emetic are mixed under different conditions of concentration and in presence of ammonia and of sodium acetate. The action is found to depend on the order in which the two solutions are mixed; thus, when a 1 per cent. solution of tannin (2—3 mols.) is added to 1 per cent. tartar emetic solution (1 mol.), a precipitate is obtained, whilst if the solutions are mixed in the inverse order, no precipitate is formed. The precipitate obtained is in every case white and gelatinous, giving greyish lumps when dried in a desiccator. When dried at the ordinary temperature, the composition corresponds with the formula  $\text{C}_{14}\text{H}_9(\text{SbO})\text{O}_9\cdot\text{H}_2\text{O}$ , but if dried at  $100^\circ$  the formula is  $\text{C}_{14}\text{H}_9\text{SbO}_9$ . The filtrate from the precipitate always gives the reactions for antimony and for tannin. T. H. P.

**Action of Benzenediazonium Chloride on Methylenedi-2-hydroxy-3-naphthoic Acid.** By ERICH STROHBACH (*Ber.*, 1901, 34, 4162—4165. Compare Möhlau and Strohbach, Abstr., 1900, i, 368).—The basic sodium salt,  $\text{CH}_2[\text{C}_{10}\text{H}_5(\text{ONa})\cdot\text{CO}_2\text{Na}]_2\cdot 2\text{H}_2\text{O}$ , of methylenedi-2-hydroxy-3-naphthoic acid, obtained by treating the acid with an alcoholic solution of sodium ethoxide, crystallises in pale yellow needles.

The methylene radicle of methylenedi-2-hydroxy-3-naphthoic acid is displaced by two azo-residues when benzenediazonium chloride is added

to an alkaline solution of the acid, the product being identical with von Kostanecki's 1-benzeneazo-2-hydroxy-3-naphthoic acid (Abstr., 1894, i, 91).  
G. T. M.

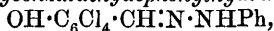
**Chlorination of *m*-Hydroxybenzaldehyde.** By HEINRICH BILTZ and OTTO KAMMANN (*Ber.*, 1901, 34, 4118—4128. Compare Zincke and Walbaum, Abstr., 1891, 708).—*Aldehydotrichloroquinodichloride*,

$\begin{array}{c} \text{CCl}\cdot\text{CO}-\text{CCl} \\ | \quad | \\ \text{CCl}\cdot\text{CCl}_2\cdot\text{C}\cdot\text{CHO} \end{array}$ , prepared by saturating with chlorine an acetic acid solution of *m*-hydroxybenzaldehyde slightly diluted with water, first at the ordinary temperature and then on the water-bath, crystallises from glacial acetic acid in yellow plates, and melts at 137—138°. It is decomposed by alkali hydroxides and carbonates, and also by phenylhydrazine and aniline. The *oxime*,  $\text{C}_7\text{H}_5\text{O}_2\text{NCl}_5$ , crystallises from dilute alcohol in brownish-yellow leaflets, melts at 169°, and is readily soluble in the ordinary organic solvents. The *semicarbazone* separates in orange-coloured, cubical crystals, and melts at 202°.

*Dichloromethyltrichloroquinodichloride*,  $\begin{array}{c} \text{CCl}\cdot\text{CO}-\text{CCl} \\ | \quad | \\ \text{CCl}\cdot\text{CCl}_2\cdot\text{C}\cdot\text{CHCl}_2 \end{array}$ , produced by treating the preceding aldehyde with phosphorus pentachloride, separates in colourless crystals and melts at 117°; a bye-product containing phosphorus and melting at 224° is also formed in this reaction.

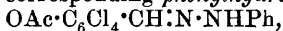
*Tetrachloro-m-hydroxybenzaldehyde*,  $\text{OH}\cdot\text{C}_6\text{Cl}_4\cdot\text{CHO}$ , obtained in quantitative yield by reducing aldehydotrichloroquinodichloride in acetic acid solution with stannous chloride, crystallises from benzene in colourless needles melting at 189—190°. The *acetyl* derivative,  $\text{OAc}\cdot\text{C}_6\text{Cl}_4\cdot\text{CHO}$ , crystallises from glacial acetic acid in needles, and melts at 112°.

*Tetrachloro-m-hydroxybenzaldehydephenylhydrazone*,



produced by mixing its generators in acetic acid solution, separates from this solvent in felted, yellow needles and melts at 124—125°. Both the phenylhydrazone and the aldehyde dissolve in solutions of the alkali carbonates and hydroxides, developing yellow colorations.

Acetyltetrachloro-*m*-hydroxybenzaldehyde, when treated with phenylhydrazine, yields the corresponding *phenylhydrazone*,



a substance crystallising in yellow plates and melting at 188—189°, which, on warming with acetic anhydride, gives rise to the *diacetate*,  $\text{OAc}\cdot\text{C}_6\text{Cl}_4\cdot\text{CH}\cdot\text{NPhAc}$ ; this compound, also obtained by acetylating tetrachloro-*m*-hydroxybenzaldehydephenylhydrazone, crystallises in light brown leaflets, and melts at 148°.

*Tetrachloro-m-ethoxybenzaldehyde*,  $\text{OEt}\cdot\text{C}_6\text{Cl}_4\cdot\text{CHO}$ , prepared by boiling together tetrachloro-*m*-hydroxybenzaldehyde, sodium ethoxide, and ethyl iodide in alcoholic solution, separates from glacial acetic acid in felted, colourless needles, and melts at 67—68°; the *phenylhydrazone* crystallises from the ordinary organic solvents in yellow leaflets melting at 111—112°.

*Tetrachloro-m-hydroxybenzaldoxime*,  $\text{OH}\cdot\text{C}_6\text{Cl}_4\cdot\text{CH}\cdot\text{NOH}$ , produced

from hydroxylamine hydrochloride, sodium hydroxide, and the corresponding aldehyde in aqueous solution, crystallises from benzene in white needles and melts at 194—195°.

*Acetyl tetrachloro-m-hydroxybenzonitrile*,  $\text{OAc} \cdot \text{C}_6\text{Cl}_4 \cdot \text{CN}$ , obtained by heating the preceding oxime with acetic anhydride, crystallises in aggregates of lustrous, pale red needles and melts at 145—146°; when hydrolysed with a boiling alcoholic solution of sodium ethoxide, it yields the sodium derivative of *tetrachloro-m-hydroxybenzonitrile*. The latter nitrile forms yellowish-white needles and melts at 219—220°.

*Tetrachloro-m-hydroxybenzamide*,  $\text{OH} \cdot \text{C}_6\text{Cl}_4 \cdot \text{CO} \cdot \text{NH}_2$ , produced by hydrolysing tetrachloro-*m*-hydroxybenzonitrile with 10 per cent. hydrochloric acid at 200°, crystallises from glacial acetic acid in needles melting at 260—261°; on further treatment with boiling 50 per cent. sulphuric acid, the amide yields tetrachloro-*m*-hydroxybenzoic acid (m. p. 172°), this acid being also obtained by the direct oxidation of tetrachloro-*m*-hydroxybenzaldehyde.

*Tetrachloro-m-hydroxybenzylidene chloride*,  $\text{OH} \cdot \text{C}_6\text{Cl}_4 \cdot \text{CHCl}_2$ , prepared by the action of phosphorus pentachloride on tetrachloro-*m*-hydroxybenzaldehyde, crystallises from glacial acetic acid in prisms with truncated, pyramidal ends, and melts at 86—87°; it separates from the dilute acid in aggregates of needles containing  $3\text{H}_2\text{O}$  and melting at 66—68°. This chloride is also obtained by reducing dichloromethyltrichloroquinodichloride with stannous chloride, and justifies the constitution given to this quinone derivative.

*Tetrachloro-m-acetoxymethylidene chloride*,  $\text{OAc} \cdot \text{C}_6\text{Cl}_4 \cdot \text{CHCl}_2$ , produced by warming the preceding compound with acetic anhydride, crystallises from glacial acetic acid in colourless, double pyramids. G. T. M.

**Halogen Derivatives of Phenols.** By W. RICHTER (*Ber.*, 1901, 34, 4292—4296. Compare Auwers, *Abstr.*, 1899, i, 36; 1900, i, 164, 165). —*p*-Acetoxymethylidene bromide,  $\text{CHBr}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OAc}$ , obtained by the action of phosphorus pentabromide on *p*-acetoxymethylidene (b. p. 264—265°), crystallises from light petroleum in colourless prisms, melts at 97—98°, and is readily soluble in most organic solvents. It turns dark on exposure to light, and on treatment with an acetic acid solution of hydrogen bromide, even in the entire absence of moisture, yields *p*-hydroxybenzaldehyde. By the action of bromine in chloroform solution, it is converted into dibromo-*p*-hydroxybenzaldehyde.

*m*-Acetoxymethylidene bromide, obtained by the action of phosphorus pentabromide on a chloroform solution of *m*-acetoxymethylidene (b. p. 263°), is a yellow oil, which on treatment with hydrogen bromide yields *m*-hydroxybenzaldehyde; bromine transforms it into tribromo-*m*-hydroxybenzaldehyde.

The constitution of Auwers and Hampe's tetrabromotoluquinol (*Abstr.*, 1899, i, 96) has been confirmed by the preparation of a *diacetyl* derivative melting at 282—283° and by its reduction to tribromotoluquinone melting at 203—204°.

Tetrachlorotoluquinone (Gorup, *Annalen*, 1867, 143, 159) melts at 266—270°, and on reduction with sulphurous acid yields the corresponding *quinol*,  $\text{CH}_2\text{Cl} \cdot \text{C}_6\text{Cl}_3(\text{OH})_2$ ; this crystallises from acetic acid in glistening plates, melts at 228°, and is readily soluble in dilute alkalis.

The chlorine of the side chain is not readily replaceable. The *diacetate* crystallises in glistening needles melting at  $232^{\circ}$  and readily soluble in acetone.

J. J. S.

**New Reactions of Organo-metallic Compounds. Synthesis of Ketones.** By EDMOND E. BLAISE (*Compt. rend.*, 1901, 133, 1217—1218. Compare Abstr., 1901, i, 252, 317, 363).—The crystalline compounds of the type  $\text{CRR':N}\cdot\text{MgI}, \text{Et}_2\text{O}$  (*loc. cit.*), which are formed when nitriles interact with the compounds of magnesium alkyl iodides and ether, react with water yielding ketones. To prepare the ketones, it is not necessary to isolate the intermediate compounds; the nitrile (1 mol.) is added to a solution in dry ether of magnesium alkyl iodide (1.5 mols.); the mixture is heated at  $100^{\circ}$ , and then, after addition of water and the distillation of the ether, the ketone is distilled in a current of steam. The best yields are obtained with aromatic nitriles, in which the cyano-group is in the nucleus.

*o*-Tolyl ethyl ketone,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{COEt}$ , is a liquid boiling at  $219$ — $221^{\circ}$ ; its *semicarbazone* melts at  $173^{\circ}$ . Benzyl *n*-propyl ketone, prepared from butyronitrile and benzyl chloride, is a liquid, having the odour of aniseed, and boiling at  $238$ — $241^{\circ}$ ; its *semicarbazone* melts at  $84^{\circ}$ . Benzyl *isoamyl* ketone boils at  $267^{\circ}$ ; its *semicarbazone* melts at  $133^{\circ}$ . *o*-Methyldeoxybenzoin boils at  $317$ — $320^{\circ}$  under the ordinary pressure and at  $191^{\circ}$  under 21 mm. pressure; its *semicarbazone* melts at  $198^{\circ}$ . *p*-Tolyl butyl ketone melts at  $22^{\circ}$  and boils at  $266$ — $267^{\circ}$ ; its *semicarbazone* melts at  $212^{\circ}$ . *p*-Tolyl propyl ketone boils at  $248$ — $250^{\circ}$ ; its *semicarbazone* melts at  $232^{\circ}$ . *n*-Propyl *isoamyl* ketone boils at  $176$ — $178^{\circ}$ ; its *semicarbazone* melts at  $102^{\circ}$ . Ethyl propyl ketone and phenyl ethyl ketone have also been prepared by this method; their *semicarbazones* melt at  $110^{\circ}$  and  $182^{\circ}$  respectively.

K. J. P. O.

**Condensation of Acetylene Hydrocarbons with Alkyl Esters. Synthesis of Acetylenic Ketones and  $\beta$ -Ketonic Esters.** By CHARLES MOUREU and RAYMOND DELANGE (*Compt. rend.*, 1902, 134, 45—47).—Butyrylphenylacetylene,  $\text{COPr}\cdot\text{C}\cdot\text{CPh}$ , a liquid of sp. gr. 0.998 at  $0^{\circ}$  and boiling at  $135$ — $137^{\circ}$  under 9 mm. pressure, is obtained by the action of amyl butyrate on the sodium derivative of phenylacetylene in presence of ether, and treatment of the product by water. When hydrolysed with sulphuric acid, it yields the  $\beta$ -diketone, benzoylbutyrylmethane (phenyl propyl methylene diketone), the copper derivative of which crystallises from alcohol in prisms melting at  $132$ — $133^{\circ}$ . Benzoylphenylacetylene,  $\text{COPh}\cdot\text{C}\cdot\text{CPh}$ , which melts at  $49.5^{\circ}$  and boils at about  $200^{\circ}$  under 15 mm. pressure, is obtained similarly from ethyl benzoate and phenyl acetylene; when hydrolysed, it yields dibenzoylmethane, melting at  $81^{\circ}$ .

The alkyl esters of  $\beta$ -ketonic acids are readily obtained by the action of ethyl, isopropyl, isobutyl, and amyl acetates and amyl butyrate on the sodium derivative of heptylidene. *iso*Propyl *acetoacetate* boils at  $75^{\circ}$  under 15 mm. pressure, and its copper derivative melts at  $175^{\circ}$ ; *amyl butyrylbutyrate* boils at  $125$ — $127^{\circ}$  under 9 mm. pressure.

According to the author, a complex sodium derivative such as  $\text{OEt}\cdot\text{CPh}(\text{ONa})\cdot\text{C}\cdot\text{CPh}$  is first formed, and this, in contact with water, yields the acetylenic ketone, alcohol, and sodium hydroxide. In the

case of  $\beta$ -ketonic esters a still more complex disodio-derivative is the first product (compare Abstr., 1901, i, 581 and 442). C. H. B.

**Cotoin.** By JACQUES POLLAK (*Monatsh.*, 1901, 22, 996—1001).—Cotoin yields a mononitroso-derivative and has therefore the constitution  $\text{COPh}\cdot\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{OMe}$  [ $\text{COPh}:\text{OH}:\text{OH}:\text{OMe}=1:2:6:4$ ], and not  $[1:2:4:6]$ , since, according to the observations of Kostanecki (*Ber.*, 1887, 20, 3133), a substance with the latter formula should yield a dinitroso-derivative.

*Nitrosocotoin* crystallises from acetic acid in dark red leaves and in glistening, orange-yellow needles, both forms melting at  $153\text{--}154^\circ$ . The needles, which lose weight over sulphuric acid, probably contain acetic acid of crystallisation. G. Y.

**Special Case of Steric Hindrance.** By ERNST BÖRNSTEIN (*Ber.*, 1901, 34, 4348—4351).—On treating *p*-toluidino-*p*-toluquinone-monotolylimide,  $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{C}_7\text{H}_5\text{O}\cdot\text{N}\cdot\text{C}_7\text{H}_7$  (Abstr., 1901, i, 375), with hydroxylamine hydrochloride and sodium carbonate in the presence of alcohol, a reaction takes place in which the group  $(:\text{NOH})$  replaces the group  $\text{C}_7\text{H}_7\text{N}^+$ , and *p*-toluidine and the *mono-oxime* of *p*-toluidino-*p*-toluquinone,  $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{C}_7\text{H}_5\text{O}\cdot\text{NOH}$ , are formed. The oxime crystallises in yellowish-red, lustrous leaflets melting at  $190^\circ$ , soluble in alkali hydroxides and carbonates. Concentrated hydrochloric acid dissolves it with a bluish-violet coloration, and concentrated sulphuric acid with a green coloration which becomes violet on the addition of water. K. J. P. O.

**Borneol- and Menthol-glycuronic Acids.** By A. BONANNI (*Beitr. chem. Physiol. Path.*, 1901, 1, 304—309).—See this vol., ii, 160.

**Colophony.** By WILHELM FAHRION (*Zeit. angew. Chem.*, 1901, 14, 1197—1208, 1221—1233, 1252—1253).—The colophony used was of American origin. The acid number obtained was 170.2, the saponification number 177.9, the difference (7.7) being the ether number.

Colophony is partially soluble in light petroleum, and the author understands by "inner acid or saponification number" the quantity of potassium hydroxide, expressed in milligrams, required for the neutralisation or saponification of 1 gram of the soluble portion. The numbers obtained were 162.7 and 164.3 respectively; whilst in another series, the "inner saponification number" was 165.2. The inconsistency of this leads to the conclusion that the portion of colophony soluble in light petroleum does not contain an ester, but another neutral saponifiable substance.

The part insoluble in light petroleum consists essentially of an acid, which, however, in presence of excess of alkali unites with more of this than is necessary for the saturation of the carboxyl group. The amount of insoluble residue (in light petroleum) depends on the extent to which the colophony has suffered autoxidation. The colophony also contains unsaponifiable matter, so that the molecular weight of the acid cannot be calculated directly from the "inner acid number"; the quantity of unsaponifiable matter increases with the length of time that the colophony is exposed to the air. After

determining the percentage of acid in the portion soluble in light petroleum, the molecular weight calculated from the "inner acid number" is about 313. This agrees with the formula  $C_{20}H_{30}O_2$  for sylvic acid. It is proved that crystallised sylvic acid is identical with abietic acid, and Mach's formula,  $C_{19}H_{28}O_2$ , is incorrect. The melting point of crystallised sylvic acid varies considerably ( $148^\circ$  to  $164^\circ$ ) according to the method of heating. The constitution suggested

by Bischoff and Nastvogel, namely,  $\begin{array}{c} \text{CH}_2\text{C}(\text{CO}_2\text{H})\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}=\text{CH} \\ \text{CH}_2-\text{CHPr}-\text{CH}\cdot\text{CH}\cdot\text{CHPr}-\text{CH}_2 \end{array}$ ,

seems to satisfactorily express its reactions towards alkali and iodine respectively. The sylvic acid contained in the colophony is in an amorphous condition, and from the fact that crystallised sylvic acid gives an ethyl ester, it is probable that the above constitution represents the amorphous variety, and in the crystallised the carboxyl group lies further away from the doubly linked carbon atoms. From the amorphous sylvic acid, the crystallised modification can be obtained by treatment with aqueous alcohol or by the action of hydrochloric acid on the alcoholic solution. The melting point of the amorphous acid is not very definite, but lies considerably below that of the crystallised. By prolonged heating of the crystallised acid, it is converted into the amorphous variety, and at the same time the molecular weight (calculated from the acid value) is increased because some other products are formed; in fact, colophony is produced, and this leads to the view that the turpentine contains sylvic acid, and as the terpenes only distil at a comparatively high temperature, this serves to convert the acid into colophony.

Sylvic acid is autoxidisable; a peroxide,  $C_{20}H_{30}O_6$ , is formed, and this is transformed by intramolecular rearrangement into *tetraoxy-sylvic acid*,  $C_{20}H_{28}(OH)_2O_4$ . The autoxidation, however, takes place in stages, and a peroxide of the formula  $C_{20}H_{30}O_4$  is first produced, which is transformed into *dioxysylvic acid*,  $C_{20}H_{29}(OH)O_3$ .

The part of the colophony insoluble in light petroleum contains these peroxides. When oxidised with permanganate in alkaline solution, sylvic acid gives an acid which is probably *tetrahydroxysylvic acid*,  $C_{20}H_{32}(OH)_4O_2$ .

Incidentally, the author has investigated the iodine value of certain phenols, quinones, and peroxides, and concludes that for these it is quite worthless, and for substances in general containing hydroxyl groups its value is always doubtful.

J. McC.

**The Resins of Copaiva Balsams.** By [ALEXANDER TSCHIRCH and] EDUARD KETO (*Arch. Pharm.*, 1901, 239, 548—581).—Copaiva balsams from Maracaibo and Para were examined; also an African variety, illurin balsam, obtained from *Hardwickia Mannii* in the Niger basin. The balsam was diluted with ether, and extracted completely with 5 per cent. aqueous sodium carbonate, and then a few times with 1 per cent. aqueous potassium hydroxide. From the residue, the ether was distilled off, and the *essential oil* distilled over with steam; there remained a mixture of indifferent *resens*, mostly, but not wholly, soluble in alcohol. These are present in but small amount, whereas the oil forms the chief constituent of the balsam.



The resin acids were liberated from the sodium carbonate solution with hydrochloric acid, and redissolved in ether; the solution was extracted first with 5 per cent. aqueous ammonium carbonate, then with 5 per cent. aqueous sodium carbonate. In the case of the Para balsam, there were obtained: from the ammonium carbonate solution, *para-copaivic acid*,  $C_{20}H_{32}O_3$ , melting at  $145-148^\circ$ , and from the sodium carbonate solution, *homoparacopaivic acid*,  $C_{18}H_{28}O_3$ , melting at  $111-112^\circ$ . From samples of Maracaibo balsam,  $\beta$ -*metacopaivic acid*,  $C_{17}H_{26}O_2$  (or  $C_{16}H_{24}O_3$  or  $C_{22}H_{32}O_4$ ), melting at  $89-90^\circ$ , and *illuric acid*,  $C_{20}H_{28}O_3$ , melting at  $128-129^\circ$ , were obtained. From illurin balsam, illuric acid was obtained. The amount of the resin acids varies from 10 per cent. of the balsam in the case of the Para variety to 30-40 per cent. in the case of that from Maracaibo. In the case of the Para balsam, about equal amounts of the acids dissolve in the ammonium and sodium carbonate solutions; in the other cases but little dissolved in the ammonium carbonate. Only a small part of the acids could be obtained crystalline, the bulk being amorphous and not entirely soluble in light petroleum.

One sample of illurin balsam contained a crystalline sediment consisting of illuric acid; in consequence, this acid could be isolated in comparatively large amount and its properties studied. It crystallises in the hexagonal system and has  $[\alpha]_D -58.9^\circ$  in 5 per cent. alcoholic solution at  $18^\circ$ . It is a monobasic acid; its crystalline *barium* (with  $4H_2O$  ?), *sodium* (with  $6H_2O$  ?), and *lead* salts and its amorphous *silver* salt were analysed. It does not contain a methoxyl or ethoxyl group; it will not form an acetyl or benzoyl derivative, or a methyl or ethyl derivative; it will not react with hydroxylamine or phenylhydrazine; with phosphorus pentachloride or triiodide, it does not yield a well defined product; with alcoholic hydrochloric acid, it does not yield an ester, but is transformed into an isomeric *acid*,  $C_{20}H_{28}O_3$ , melting at  $108-109^\circ$ ; it reacts with nitric acid, and also with sulphuric acid, but the respective products do not contain nitrogen or sulphur. The acid has an iodine number corresponding with the presence of two double linkings, and in alcoholic solution it takes up 4 atoms of bromine. It gives the cholesterol reactions and is not affected by fusion with potassium hydroxide; in these and other respects it resembles the resin acids of the *Coniferae*, especially pimaric acid, but it differs from them in that it reduces silver salts in alkaline solution. It resists the action of reducing agents, but it can be oxidised; excess of alkaline permanganate converts it into carbonic, oxalic, formic, acetic, and other fatty acids, together with a small quantity of an acid which melts at  $194^\circ$ . Illuric acid is probably identical with the acid obtained by Umney and by Peinemann from illurin balsam; possibly, also with Fehling's oxy-copaivic acid. Schweitzer-Rose's copaivic and Strauss's meta-copaivic acids could not be obtained from the balsam.

A commercial specimen of "copaivic acid" appeared to be identical with metacholestol (Mach, Abstr., 1895, i, 384). C. F. B.

**Constituents of Koso Flowers.** By [RUDOLF BOEHM and] ARTHUR LOBECK (*Arch. Pharm.*, 1901, 239, 672-696. Compare Leichsenring, Abstr., 1894, i, 424; Dacomo and Malagnini, Abstr., 1899, i, 158).—By repeated crystallisation from alcohol, commercial

kosin was separated into less soluble  $\alpha$ -kosin melting at  $160^\circ$ , and a little  $\beta$ -kosin, more soluble in alcohol, and melting at  $120^\circ$ ; both have the constitution  $C_{21}H_{24}O_5(OMe)_2$  or  $C_{20}H_{20}O_5(OMe)_2$ .  $\alpha$ -Kosin forms a tribenzoyl derivative,  $C_{20}H_{17}O_2(OBz)_3(OMe)_2$  or  $C_{21}H_{21}O_2(OBz)_3(OMe)_2$ ; when heated with 10 per cent. aqueous sodium hydroxide and zinc dust, it is attacked, but only slightly, some methylphloroglucinol methyl ether (compare Boehm, Abstr., 1899, i, 32) being formed; when it is heated for a few minutes with strong sulphuric acid, the same product is obtained in 14 per cent. yield, together with butyric acid.

A commercial ethereal extract of *Flores Koso* was examined by pounding it with calcined magnesia, extracting the mixture with water, and precipitating the extract with dilute sulphuric acid. From a solution of the crude product in methyl alcohol, a little *anhydroprotokosin*,  $C_{58}H_{74}O_{17}$ , crystallised slowly; this melts at  $182^\circ$  and, when crystallised from alcohol containing a little water, is converted into Leichsenring's protokosin,  $C_{29}H_{38}O_9$ , which contains two methoxyl groups and is thus  $C_{27}H_{32}O_7(OMe)_2$ . From the mother liquor, by evaporation and treatment with light petroleum, small quantities of *kosidin*,  $C_{29}H_{40}O_9(OMe)_2$ , melting at  $178^\circ$ , were obtained. The main constituent, however, was kosotoxin, which melted at  $62^\circ$ , and probably has the formula  $C_{50}H_{62}O_{18}(OMe)_2$ , rather than half this, since all the other constituents of the drug contain 2 methoxyl groups in the molecule. When heated with aqueous sodium hydroxide and zinc dust, kosotoxin is, to a large extent, converted into kosin, but some trimethylphloroglucinol and dimethylphloroglucinol are formed also. When heated with strong sulphuric acid for a little while, it yields some trimethylphloroglucinol and methylphloroglucinol methyl ether.

Different samples and extracts of the flowers were found to differ greatly. From one sample of the flowers, a little of a poisonous substance,  $\alpha$ -kosotoxin, was obtained, which melts at  $68$ – $69^\circ$  and seems to have the constitution  $C_{24}H_{34}O_8(OMe)_2$ . From a sample of ethereal extract, a microcrystalline substance was obtained which burns on platinum foil without melting, contains methoxyl, and has the composition  $C_{19}H_{12}O_{10}$ .  
C. F. B.

**A Blue Pigment from Crenilabrus Pavo.** By RICHARD VON ZEYNEK (*Zeit. physiol. Chem.*, 1901, 34, 148–152).—A deep blue pigment can be extracted by means of glycerol from the floats of *Crenilabrus pavo*. Its solubilities and optical properties are described; it is not yet identified chemically.  
W. D. H.

**Guaiacum Blue and Aloin Red.** By EDUARD SCHAER (*Verh. Natur.-Gesell. Basel*, 1901, 13, 287–307. Compare Abstr., 1900, i, 512; ii, 583).—Schönbein has suggested that the blue substance formed by oxidising 'guaiaconic acid' from guaiacum resin is a peroxide similar to ozone. In accordance with this view, it is now shown that the blue colour is very readily destroyed by a number of chemical agents and is also sensitive to the action of light. The influence of acids is determined by their strength; sulphuric, hydrochloric, and salicylic acids act the most powerfully, then tartaric, citric, and formic acids, whilst benzoic and acetic acids have only a feeble action; when

dissolved in solvents not miscible with water, the blue colour is only very slightly sensitive to the action of acids. Alkali hydroxides and carbonates and alkaline salts act much more vigorously than acids; they quickly destroy the blue colour when formed, and entirely prevent its formation by the oxidation of guaiacum resin or guaiaconic acid. The action of light greatly facilitates the formation of guaiacum blue by the atmospheric oxidation of guaiacum resin or of the acid prepared from it, but it is also very active in bringing about the subsequent spontaneous bleaching of the blue colour; both these processes are regarded as oxidations in which the oxygen of the air is rendered active by the resin and other constituents of the solution.

It is pointed out that the formation of 'aloin-red' from 'barbaloin' proceeds in a manner very similar to that of 'guaiacum-blue' from guaiacum resin, and five methods of producing this red compound are described, including two in which peroxides are probably the active agents; its formation may be used as a very sensitive test for aloë preparations, for cyanogen and halogen compounds (especially hydrocyanic acid), for free ammonia, for copper, and for peroxides.

T. M. L.

**Basic Properties of Oxygen.** By PAUL WALDEN (*Ber.*, 1901, 34, 4185—4202. Compare Collie and Tickle, *Trans.*, 1899, 75, 710; Kehrmann, *Abstr.*, 1900, i, 61; 1901, i, 484; von Baeyer and Villiger, *Abstr.*, 1901, i, 658, and this vol., i, 112; Werner, this vol., i, 50).—The early part of this paper consists of an historical summary; the latter part is a physico-chemical study of dimethylpyrone. This substance has no appreciable influence on the speed of mutarotation of sucrose; if a base, it is a very much weaker one than aniline. The values for the distribution ratios between benzene and water, of picric acid alone, and of picric acid along with dimethylpyrone (1 mol.) show that in concentrated solutions ( $v=32$ ) a dimethylpyrone picrate is formed which is decomposed into its constituents by dilution. From the difference in the depression of the freezing point of dilute solutions of hydrochloric acid caused by the addition of dimethylpyrone, the affinity constant,  $k_b$ , of the latter as a base is found to be approximately  $3 \times 10^{-14}$ .

Dimethylpyrone comports itself as a relatively good electrolyte in liquid sulphur dioxide at  $0^\circ$ ; the conductivity increases on dilution, owing, probably, to dissociation of the salt formed into the ions  $\bar{\text{S}}\bar{\text{O}}_2$  and  $\text{C}_7\text{H}_8\text{O}_2^+$ . Both dimethylpyrone and tribromoacetic acid are very feeble conductors when dissolved separately in acetonitrile, but the combination of the two in molecular proportions in concentrated solution has a considerable conductivity. Formation of a salt obviously occurs, but the rapid diminution of conductivity with dilution indicates that it has little stability. The conductivity of dimethylpyrone in aqueous solution is very slight;  $\mu_D=202$  at  $25^\circ$  approximately, and  $k=7.5 \times 10^{-9}$ .

From measurements of the conductivity of aqueous solutions of picric acid at  $25^\circ$ , and of aqueous solutions of picric acid (1 mol.) + dimethylpyrone (1 mol.) diluted (1) with water, (2) with an  $N/64$

solution of dimethylpyrone, the affinity constant,  $k_b$ , of dimethylpyrone, as a base was found to be  $2.4 \times 10^{-14}$ , a value agreeing closely with that obtained by the freezing point method (*supra*). Dimethylpyrone is thus stronger than carbamide and much weaker than aniline. The influence of dimethylpyrone on the conductivity of aqueous solutions of sodium hydroxide shows that it is not only a base but also an acid with an affinity constant  $k_a = 0.88 \times 10^{-14}$ ; it is therefore of an amphoteric character, and capable of forming both hydrogen and hydroxyl ions. The high value of  $k$  obtained with aqueous solutions of dimethylpyrone corresponds in reality to the formation of an "internal salt."

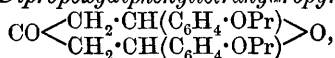
W. A. D.

**Oxygen Bases.** By JAMES WALKER (*Ber.*, 1901, 34, 4115—4118. Compare Baeyer and Villiger, *Abstr.*, 1901, i, 658).—In order to ascertain the strength of the oxygen bases, dimethylpyrone and tetramethylpyrone, each of these compounds was dissolved in the equivalent amount of  $N/10$  hydrochloric acid, and 20 c.c. of the solution were mixed with 1 c.c. of methyl acetate in a thermostat at  $35^\circ$ . The course of the hydrolysis was followed by titrations with standard barium hydroxide solution, and a comparative experiment was made with carbamide. The calculated velocity coefficient showed that these bases have approximately the same strength, the values of the constant for carbamide, dimethylpyrone, and tetramethylpyrone being 0.00066, 0.00065, and 0.00068 respectively. The hydrolytic experiments carried out in dilute solutions of varying concentration show that the hydrochlorides of carbamide and dimethylpyrone are dissociated to approximately the same extent in isotonic solutions.

Ethylene oxide is often stated to be a strong base, because it is capable of displacing metallic radicles from their salts when dissolved in water. This reaction takes place, however, only when the hydroxide thereby produced is insoluble. The first phase of the action is the hydrolytic dissociation of the dissolved metallic salt into free acid and free basic hydroxide. The equilibrium is destroyed by the addition of ethylene oxide, which absorbs some of the acid, and causes further hydrolysis of the salt, the reaction taking place in accordance with the equation  $C_2H_4(OH)Cl + M \cdot OH \rightleftharpoons C_2H_4O + H_2O + MCl$ . A certain amount of the hydroxide must be present in solution to maintain the equilibrium, and if the substance is very insoluble the required proportion is not attained and the decomposition continues until the whole of the metallic radicle is precipitated. If the salt is only slightly hydrolysed, the precipitation is very slow, as in the case of magnesium chloride; alumina, however, is rapidly thrown down, because its salts are almost completely dissociated in aqueous solution.

G. T. M.

**Double Compounds of the Oximes of Tetrahydropyrone Derivatives.** By A. POSNIAKOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 667—669).—*o*-Dipropoxydiphenyltetrahydropyrone,



prepared by a method analogous to that employed by Petrenko-Kritschenko for obtaining the corresponding *o*-diethoxy-compound

(see Abstr., 1899, i, 440), separates from alcohol in crystals melting at 112—113°. Its *oxime* is deposited in white crystals which melt at 170° and dissolve in alcohol but do not combine with it; with acetic acid, it yields a crystalline compound melting and decomposing at about 165°; the oxime also combines with chloroform and with ethylene glycol, giving well-formed crystals, but none of these compounds gives concordant results on analysis. Pyridine and quinoline also dissolve the oxime, but do not combine with it.

Petrenko-Kritschenko's supposition, that an increase in the size of the alkoxy-groups present in these derivatives heightens their capacity for combining with solvents, is thus seen to be erroneous (compare also Petrenko-Kritschenko, Abstr., 1900, i, 306).

The melting points of the dimethoxy-, diethoxy-, and dipropoxy-compounds are 202°, 133°, and 170° respectively. T. H. P.

**New Transformation of the two Xanthhydrols into Xanthenes.** By ROBERT FOSSE (*Compt. rend.*, 1901, 133, 880—882).—*Dinaphthoxanthhydrol*,  $O\langle\begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix}\rangle CH\cdot OH$ , obtained by treating bromodinaphthoxanthene,  $O\langle\begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix}\rangle CHBr$ , with an alcoholic solution of potassium hydroxide, crystallises in colourless needles and melts at 144°. When fused, this substance yields the corresponding *ether*,  $(C_{21}H_{11}O)_2O$ , a compound melting at 250°.

Dinaphthoxanthhydrol and xanthhydrol,  $O\langle\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}\rangle CH\cdot OH$ , when treated with fuming hydrochloric or hydrobromic acid, regenerate the corresponding chloro- or bromo-xanthen.

These xanthen derivatives containing a halogen behave like the salts of amines, giving rise to double salts with mercuric and platinic chlorides (compare Collie, *Trans.*, 1900, 76, 1114). The haloid xanthen derivatives, when boiled with absolute alcohol, behave like diazonium salts, exchanging their halogen for hydrogen with formation of acetaldehyde and the corresponding halogen acid. G. T. M.

**Basic Properties and Quadrivalence of Oxygen in the Xanthone Series.** By ROBERT FOSSE (*Compt. rend.*, 1901, 133, 1218—1220. Compare Abstr., 1901, i, 604, 643; and this vol., i, 51).—From a solution of dinaphthoxanthone in acetic acid and platinic chloride, a *platinichloride*,  $CH_2\cdot(C_{10}H_6)_2\cdot O\cdot PtCl_4$ , is obtained as a bright red, crystalline precipitate. The opinion is expressed that in the mono-halogenated naphthoxanthenes previously described (*loc. cit.*) the oxygen atom is quadrivalent, and that the monochloro-derivative is represented by the formula  $C_6H_4\langle\begin{smallmatrix} CH \\ O-Cl \end{smallmatrix}\rangle C_6H_3$ . The fact that this compound behaves as a hypochlorite is thus accounted for.

K. J. P. O.

**Xanthenes from 2-Hydroxy-3-naphthoic Acid. Formation of Xanthenes.** By ERICH STROHBACH (*Ber.*, 1901, 34, 4136—4146).—*Phenyl 2-hydroxy-3-naphthoate*,  $OH\cdot C_{10}H_6\cdot CO_2Ph$ , prepared by heat-

ing a mixture of phenol, 2-hydroxy-3-naphthoic acid, and phosphorus oxychloride at 130°, crystallises from dilute alcohol in leaflets melting at 128—129° and boiling at 257—261° under 160 mm. pressure. The *acetyl* derivative,  $\text{OAc} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CO}_2\text{Ph}$ , obtained from the preceding compound by Liebermann's method, melts at 186·5°.

*p*-Tolyl 2-hydroxy-3-naphthoate,  $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CO}_2 \cdot \text{C}_6\text{H}_4\text{Me}$ , crystallises in pale yellow needles, and melts at 90—90·5°; it is readily soluble in the ordinary organic solvents.

The phenyl ester, when heated at its boiling point, evolves phenol and yields  $\gamma$ -dinaphthoxanthone; the *p*-tolyl derivative under these conditions condenses without elimination of *p*-cresol to form 2-methyl- $\gamma$ -phenonaphthoxanthone, a substance separating from glacial acetic acid in pale yellow crystals and melting at 158—159°.

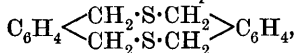
The communication also contains a discussion of syntheses in the xanthone series which is not suitable for abstraction. G. T. M.

**Heterocyclic Compounds.** By ARTHUR KÖTZ and OTTO SEVIN (*J. pr. Chem.*, 1901, [ii], 64, 518—529).—A summary is given of the methods which have been employed in the preparation of ring-compounds containing carbon and sulphur.

*m*-Xylylene disulphide,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{S} \\ \text{CH}_2 \cdot \text{S} \end{smallmatrix}$ , is a white, amorphous substance which melts at 115—116°. *p*-Xylylene disulphide is a white, amorphous substance, and melts at 168—169°.

*o*-Xylylenethiol condenses with methylene iodide to form the *o*-mercaptal,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{S} \\ \text{CH}_2 \cdot \text{S} \end{smallmatrix} \text{CH}_2$ , which separates from chloroform in thick, transparent, odourless crystals and melts at 152—153°. The *m*-mercaptal is a white, amorphous, odourless powder, melts at 73°, and is soluble in chloroform. The *p*-mercaptal is a white, amorphous, odourless powder, and melts at 149—150°.

*p*-Xylylenethiol condenses with ethylene bromide to a white, amorphous compound,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \end{smallmatrix}$ , which melts at 113—114°, and is insoluble in most solvents, but dissolves readily in chloroform. The compound  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \end{smallmatrix} \text{CH}_2$  is a white, amorphous compound, and melts at 55—56°. The compound



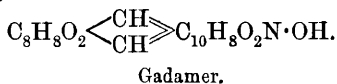
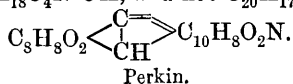
from *p*-xylylenethiol and *p*-xylylene bromide, melts at 192—193° and is insoluble in all solvents; molecular weight determinations in nitrobenzene and chloroform solutions gave values corresponding with the formula  $(\text{C}_{16}\text{H}_{14}\text{S}_2)_3$ . T. M. L.

**Gaze's "Pure Berberine."** By HARRY M. GORDIN and C. G. MERRELL (*Arch. Pharm.*, 1901, 239, 626—637).—The substance obtained by boiling acetoneberberine with chloroform and alcohol is not berberine, as Gaze supposed (*Abstr.*, 1890, 1011), but berberine hydrochloride,  $\text{C}_{20}\text{H}_{17}\text{O}_4\text{N} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ . Berberine appears to act on chloroform as alkaline mineral bases do, converting it into hydrochloric and

formic acids. Piperidine, which resembles berberine in absorbing carbon dioxide from the air, has the same action on chloroform; hydrastine, quinine, and morphine have not (for strychnine, compare Trowbridge, *Abstr.*, 1900, i, 187). C. F. B.

**Relationship of Canadine to Berberine.** By JOHANNES GADAMER (*Arch. Pharm.*, 1901, 239, 648—663).—When the hydrochloride of hydroberberine, which is optically inactive, is treated with half the equivalent amount of ammonium *d*-o-bromocamphorsulphonate, the salt of a lævorotatory base is precipitated along with hydroberberine, whilst a dextrorotatory base remains in solution. The former melts at 132° and has  $[\alpha]_D - 298.2^\circ$  in 1 per cent. chloroform solution; the second melts at 139—140°, although occasionally, when still impure, it melted at 132—133°, and has  $[\alpha]_D 297.4^\circ$ . A specimen of canadine melted at 132—133° and had  $[\alpha]_D - 298.0^\circ$ ; canadine seems, however, also to have been obtained with the melting point 140°. Evidently canadine is identical with the lævorotatory base obtained from hydroberberine, and hydroberberine must be either *r*- or *dl*-canadine.

It has been assumed generally that berberine is a tertiary base. Its compound with methyl iodide, however, is not a true ammonium iodide derivative, but is rather of the same nature as the compounds with chloroform, acetone, alcohol, &c. Moreover, berberine is a strong base, very different from hydroberberine and canadine. On these grounds, the author regards berberine as a quaternary ammonium base, and modifies Perkin's formula accordingly, regarding the alkaloid as  $C_{20}H_{18}O_4N \cdot OH$ , and not  $C_{20}H_{17}O_4N$ .



C. F. B.

**Hydroxycinchotone.** By W. WIDMAR (*Monatsh.*, 1901, 22, 976—982).—When boiled with moderately dilute sulphuric acid, the so-called cinchoninesulphonic acid yields a small quantity of  $\beta$ -iso-cinchonine and a base,  $C_{19}H_{24}O_2N_2$ , which the author considers to be *hydroxycinchotone* (*hydroxydihydrocinchonine*). The base melts at 268° and has  $[\alpha]_D + 200.79^\circ$  at 15°, measured in an alcohol-chloroform solution.

The *sulphate*,  $(C_{19}H_{24}O_2N_2)_2 \cdot H_2SO_4 \cdot 8H_2O$ , forms white, thick prisms which melt at 233—234°. The *hydrochloride*,  $C_{19}H_{24}O_2N_2 \cdot HCl$ , melts at 227—229°. The *platinichloride*,  $(C_{19}H_{24}O_2N_2)_2 \cdot H_2PtCl_6$ , crystallises in well-defined, rhombic plates.

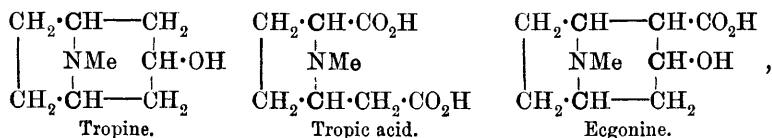
The base is quite distinct from Jungfleisch and Léger's hydroxycinchonines, and from the isomeric compound obtained by Schmid on fusing cinchotinesulphonic acid. The results agree with Skrap's suggestion (*Abstr.*, 1901, i, 404) that the substance described as cinchoninesulphonic acid is an additive compound of cinchonine and sulphuric acid. G. Y.

**Hyoscyne and Atroscine.** By JOHANNES GADAMER (*J. pr. Chem.*, 1901, [ii], 64, 566—568).—Controversial; a reply to O. Hesse (this vol., i, 51). T. M. L.

**Change of Atroscine into *i*-Scopolamine.** By HERMANN KUNZ-KRAUSE (*J. pr. Chem.*, 1901, [ii], **64**, 569—571).—Confirmation is given by melting point determinations of Gadamer's statement that dry atroscine passes spontaneously into *i*-scopolamine (*Abstr.*, 1898, i, 91). T. M. L.

**Ibogine.** The Active Principle of a Plant of the *Tabernæmontana* Genus growing in the Congo. By ALBIN HALLER and EDOUARD HECKEL (*Compt. rend.*, 1901, **133**, 850—853. Compare Dybowski and Landrin, this vol., i, 114).—*Ibogine*,  $C_{26}H_{32}O_2N_2$ , the active principle of various species of *Iboga* (*Aboua*) growing in the Congo, is extracted from the bark of the stems and roots and also from the leaves of these plants by alcohol, the macerated material having been first digested with hot light petroleum and with chloroform; it crystallises in orthorhombic forms, melts at  $152^\circ$ , and has  $[\alpha]_D -12.88^\circ$ . The alkaloid has a bitter taste and is alkaline to litmus; it is insoluble in water but dissolves in the ordinary organic solvents. The salts of the alkaloid are amorphous, and the substance is not hydrolysed on boiling it with dilute sulphuric acid. Its alcoholic solutions do not reduce Fehling's solution or ammoniacal silver nitrate. The product, when derived from the stems of the plants, is accompanied by another substance melting at  $206-207^\circ$ . G. T. M.

**Tropic Acids and the Optical Function of the Asymmetric Carbon Atoms in Tropine and Ecgonine.** By JOHANNES GADAMER (*Arch. Pharm.*, 1901, **239**, 663—671).—It is known that tropine yields an optically inactive tropic acid when oxidised, whereas both *d*- and *l*-ecgonine (these are not optical antipodes) yield an active *d*-tropic acid.



As even tropine from hyoscyamine is optically inactive, and as naturally occurring compounds with asymmetric carbon atoms are usually active and not mixtures of optical antipodes, it is probable that tropine is inactive by internal compensation, its two similar asymmetric carbon atoms (printed in thicker type in the formula) being respectively *d* and *l*. By oxidation to tropic acid, the symmetry of the molecule is destroyed, and the two asymmetric carbon atoms are no longer similar. The inactive tropic acid thus obtained is therefore probably susceptible of resolution into active components. The author has effected this resolution by crystallisation of the cinchonine salt from a mixture of alcohol and acetone. From the less soluble portion, *l*-tropic acid was prepared with  $[\alpha]_D -14.8^\circ$  to  $-15.2^\circ$  in 2—6.5 per cent. aqueous solution at  $20^\circ$ , and melting point  $243^\circ$ ; the ammonium salt had  $[\alpha] +16.5^\circ$  in 3 per cent. aqueous solution at  $20^\circ$ . From the mother liquor of the insoluble cinchonine salt *d*-tropic acid was obtained, but only in the impure state, with  $[\alpha]_D +7.4^\circ$  in 14 per cent. aqueous



solution at 20°. As tropic acid from ecgonine has  $[\alpha]_D +14.9^\circ$  to  $+15.1^\circ$  (Liebermann, Abstr., 1891, 749), it is presumably identical with *d*-tropic acid from tropine, and consequently the two left-hand asymmetric carbon atoms in ecgonine must be respectively *d*- and *l*-, as in tropine and the tropic acid obtained from it.

The author also discusses the nature of the two other asymmetric carbon atoms in ecgonine. C. F. B.

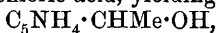
**Ferrous Chloride Pyridine.** By PAUL PFEIFFER (*Zeit. anorg. Chem.*, 1901, 29, 138—139).—Chromium chloride pyridine (Abstr., 1900, i, 559), when heated with iron, gives large, greenish, transparent crystals, which become yellowish when pulverised. The substance is probably identical with the compound,  $\text{FeCl}_2 \cdot 3\text{C}_5\text{NH}_5 \cdot 2\text{H}_2\text{O}$ , described by Reitzenstein (Abstr., 1900, i, 162), as the ratio of  $\text{Fe}:\text{Cl}:\text{C}_5\text{NH}_5$  has been found to be nearly 1 : 2 : 3. J. McC.

**2- and 4-Benzoylpyridines and their Derivatives.** By A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 700—707).—The oxidation of 2- and 4-benzylpyridines to the corresponding benzoylpyridines is best effected by means of potassium permanganate in neutral solution, the yields obtained reaching about 90 per cent.

*2-Benzoylpyridine*,  $\text{COPh} \cdot \text{C}_5\text{H}_4\text{N}$ , obtained as a liquid boiling at 317° under 763 mm. pressure, dissolves in water, alcohol, or ether, does not solidify when cooled in ice and salt, and has the sp. gr. 1.1558 at 20°/0° and 1.1710 at 0°/0°. It has feeble basic properties, and dissolves in mineral acids, but all its salts are hydrolysed by large proportions of water with the separation of the base as an oil. The *platinichloride*,  $(\text{C}_{12}\text{H}_9\text{ON})_2 \cdot \text{H}_2\text{PtCl}_6$ , crystallises from water, by which it is partially decomposed, in the form of aggregates of yellow crystals. The *picrate*,  $\text{C}_{12}\text{H}_9\text{ON} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , separates from alcohol or acetone in short prisms with rhombic bases melting at about 130° with slight decomposition. The *phenylhydrazone*,  $\text{C}_{13}\text{H}_{15}\text{N}_3$ , is deposited from alcohol in faintly yellow crystals melting at 136—137°. *2-Benzoylpyridine* yields two isomeric *oximes*, which are formed simultaneously but can be readily separated by crystallisation, since one form is deposited in cubes melting at 150—152° whilst the other isomeride is obtained as tetrahedra melting at 165—167°. If a large excess of hydroxylamine is employed, the cubic modification is obtained in predominating proportion. The configurations of the two forms were not determined.

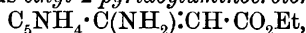
*4-Benzoylpyridine* crystallises from light petroleum in thin plates melting at 72° and boils at 315° under 762 mm. pressure; it is soluble in water, alcohol, or ether, and also in mineral acids, yielding salts which are readily decomposed by water. The *platinichloride* separates in needles and is completely decomposed by water; the *picrate* crystallises from alcohol in feathery aggregates, which melt and slightly decompose at 160° and are soluble in acetone. The *phenylhydrazone* separates from alcohol in faintly yellow crystals melting at 181—182°. Two *oximes* were also obtained in this case, the one obtained in the larger quantity separating from alcohol in prisms melting at 176—177°, whilst the other forms small crystals melting at 152—155°. No trace could be found of the oxime melting at 163—165, described by Freund (Abstr., 1898, i, 43) and by Fulda (Abstr., 1900, i, 53). T. H. P.

**Esters of Pyridoylacetic Acids.** By ADOLF PINNER [and M. DONCHI, PAUL DREXLER, and B. BAY] (*Ber.*, 1901, **34**, 4234—4253).—A detailed description of the pyridoylacetaes (see Abstr., 1900, i, 409). These, when treated with hydrochloric acids, yield the ketones  $C_5NH_4 \cdot COMe$ , which, like the ketonic acids, easily form oximes, hydrazones, and pyrazolones. The cyanohydrins of the ketones decompose when treated with hydrochloric acid, yielding carbinols,



which reduce Fehling's solution in the cold.

Ethyl 2-pyridoylacetate decomposes when distilled, but forms stable salts; the *sodium* derivative crystallises in needles and melts and decomposes at  $234^\circ$ ; the *potassium* and *copper* derivatives also crystallise in needles, the *hydrochloride*, *sulphate*, and *nitrate* are unstable, but the *platinichloride* crystallises in thick, red plates and melts at  $175^\circ$ . The *phenylhydrazone* crystallises from methyl alcohol in long, lustrous, yellowish needles, melts at  $122^\circ$ , and forms a *picrate* which crystallises in yellow, felted needles melting at  $197^\circ$ . 3-*a*-Pyridoyl-1-phenylpyrazolone,  $N \begin{smallmatrix} \diagup C(C_5NH_4) \\ \diagdown NPh-CO \end{smallmatrix} > CH_2$ , crystallises from benzene in small nodules and melts at  $179^\circ$ ; the potassium derivative of ethyl 2-pyridoylacetate, when oxidised by iodine, yields *ethyl di-2-pyridoylsuccinate*,  $C_2H_2(CO \cdot C_5NH_4)_2(CO_2Et)_2$ , which crystallises in colourless, rhombic prisms, melts at  $137^\circ$ , and forms a *platinichloride* crystallising in red plates and melting and decomposing at  $217^\circ$ ; the ester, when treated with ammonia, yields *ethyl 2-pyridoylaminocrotonate*,

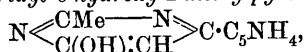


which crystallises from alcohol, melts at  $63^\circ$ , and is immediately decomposed by acids into ammonia and the acetate; the salts of the acetate react with alkyl haloids forming the alkyl esters, but these are all unstable liquids; 2-pyridyl methyl ketone forms a hygroscopic *hydrochloride* melting at  $183$ — $185^\circ$ , a *platinichloride* crystallising in prisms and melting at  $220^\circ$ , and an amorphous *nitrate* melting and decomposing at  $125^\circ$ . The corresponding *carbinol* was not obtained in the pure state, as the melting point of the recrystallised product varied, probably owing to the formation of its pinacone; it forms, however, a stable *hydrochloride* melting at  $205^\circ$ , and *platinichloride* which crystallises, with  $1\frac{1}{2}H_2O$ , in yellow prisms and melts at  $218^\circ$  when anhydrous.

The unstable *ethyl  $\beta$ -2-pyridoylpropionate*, obtained either by the condensation of ethyl  $\alpha$ -pyridinecarboxylate and ethyl propionate or by the methylation of *ethyl 2-pyridoylacetate*, forms an amorphous *platinichloride* melting at  $175^\circ$ , and when warmed with hydrochloric acid, yields 2-pyridyl ethyl ketone; the latter forms a *hydrochloride* which crystallises in small, deliquescent prisms melting at  $148$ — $150^\circ$ , and a *platinichloride* which crystallises in reddish, lustrous prisms melting at  $188^\circ$ . The analogous 2-pyridoylethylacetate easily yields 2-pyridyl propyl ketone, which forms a crystalline *picrate* melting at  $75^\circ$ . 2-Pyridyl phenethyl ketone, obtained by treating the sodium salt of ethyl 2-pyridoylacetate with benzyl chloride, is an unstable oil and forms a crystalline *platinichloride* melting at  $188^\circ$  and a *picrate* melting at  $129^\circ$ .

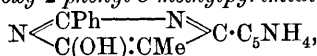
The pyridoylacetaes easily condense with amidines forming hydroxy-

pyrimidines. 4-*a*-Pyridyl-6-hydroxy-2-methylpyrimidine,



from acetamidine and ethyl 2-pyridoylacetate, crystallises from alcohol in needles, melts at 270°, and forms an amorphous, insoluble silver salt. 4-*a*-Pyridyl-6-hydroxy-2-phenylpyrimidine crystallises in needles, melts at 268°, is soluble in alkalis and mineral acids, and forms a *platinichloride* which crystallises in needles melting at 268°; the *ethyl* ether crystallises in prisms, melts at 120°, and forms a *platinichloride* melting at 205°; the *acetyl* derivative crystallises in needles melting at 150°, and, when heated, yields the *anhydride* of the hydroxypyrimidine, (C<sub>15</sub>H<sub>10</sub>N<sub>3</sub>)<sub>2</sub>O, which crystallises from alcohol in needles, and melts at 208°. This reaction seems to be a general one for the acetyl derivatives of hydroxypyrimidines.

4-*a*-Pyridyl-6-hydroxy-2-phenyl-5-methylpyrimidine,



from ethyl β-2-pyridoylpropionate and benzamidine, crystallises from alcohol in prisms melting at 230°; it forms an amorphous *platinichloride* melting at 238°, and an *acetyl* derivative which crystallises in prisms, melts at 104°, and yields an *anhydride* when heated.

Ethyl 3-pyridoylacetate forms a *potassium* salt which crystallises from acetone in needles, an amorphous *copper* salt, an amorphous *silver* salt, and a *platinichloride*.

*Ethyl 4-pyridinecarboxylate* is a colourless liquid which boils at 110° under 15 mm., and at 219–220° under atmospheric pressure, and has a sp. gr. 1·0091 at 15°; its *hydrochloride* crystallises in hygroscopic, lustrous needles and melts at 165°; its *platinichloride* is an amorphous, orange-yellow precipitate.

*Ethyl 4-pyridoylacetate* crystallises in thick bundles of prisms melting at 54°; the *sodium* and *potassium* derivatives crystallise in needles; the *copper* derivative is crystalline, and melts at 183–184°, and the *silver* derivative is amorphous; the *platinichloride* crystallises in orange-red leaflets, and melts at 156°. The *phenylhydrazone* crystallises in small needles, and, when heated, is converted into 3-*γ*-pyridyl-1-phenylpyrazolone, which crystallises from methyl alcohol, and melts at 215°; *ethyl di-4-pyridoylsuccinate* crystallises in small needles melting at 197°. 4-Pyridyl methyl ketone is an oil which boils at 212–214° and is easily soluble in alcohol, ether, or acids; its *hydrochloride* is deliquescent; the *platinichloride* crystallises in lustrous leaflets melting at 205°, the *mercurichloride* in needles melting at 183–184°, the *picrate* in leaflets melting at 130°, the *phenylhydrazone* in yellow needles melting at 150°, and the *oxime* in lustrous needles melting at 142°. When treated with methyl iodide, the sodium derivative of ethyl 4-pyridoylacetate yields the *methiodide* of 4-pyridyl ethyl ketone, which, when treated with silver chloride, is converted into the *methochloride*; the latter crystallises in very deliquescent needles, and forms a *platinichloride* which crystallises in needles, melting and decomposing at 205°, and an *aurichloride* which crystallises in yellow, lustrous plates and melts at 163–164°. 4-Pyridyl propyl ketone is an oil boiling at 229–231°, and forms a *picrate* which crystallises in long, yellow needles melting at 96°.

4-Pyridyl butyl ketone boils at 239—240°, and its *picrate* crystallises in needles melting at 101°.

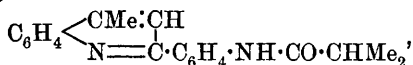
The *ethyl* ester of 2-methylpyridine-6-carboxylic acid (Abstr., 1900, i, 409) boils at 133° under 35 mm. pressure, and when treated with ethyl acetate and sodium ethoxide yields *sodium 2-methyl-6-pyridoyl-acetate* which crystallises in yellow nodules from alcohol; the *acid* is an oil which cannot be distilled, the *potassium* salt crystallises from acetone in long needles. 2-Methyl-6-pyridyl methyl ketone is a colourless oil boiling at 198—200°; it forms a *platinichloride* melting at 162°.

R. H. P.

**Ethyl Dihydroxycinchomeronate.** By SIEGFRIED RUHEMANN (*Ber.*, 1901, 34, 4165).—A claim for priority (compare *Trans.*, 1900, 67, 250, and Errera and Perciabosco, this vol., i, 116). W. A. D.

**Synthesis of 2- and 4-Hydroxyquinolines.** By RUDOLF CAMPS (*Arch. Pharm.*, 1901, 239, 591—610. Compare Abstr., 1900, i, 115, 310).—When *o*-isobutyrylaminoacetophenone (Bischler, Abstr., 1893, i, 531),  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CHMe}_2$ , is boiled with a dilute solution of sodium hydroxide in alcohol and water, 4-hydroxy-2-isopropylquinoline,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C(OH)CH} \\ \text{N}=\text{C} \cdot \text{CHMe}_2 \end{smallmatrix}$ , 3:3:4-trimethyl-2-quinolone,

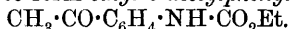
$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CMe} \cdot \text{CMe}_2 \\ \text{N}=\text{CO} \end{smallmatrix}$ , and *isobutyryl-o*-flavaniline,



are obtained, melting respectively at 196°, 143—144°, and 117°.

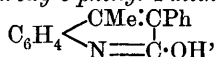
*o*-Benzoylaminoacetophenone (Bischler, *loc. cit.*), under similar circumstances, yields 4-hydroxy-2-phenylquinoline (Knorr, Abstr., 1888, 1113), together with a little *benzoyl-o*-flavaniline, which melts at 150°. That Bischler could not effect a similar condensation was due to the fact that the alcohol he employed was free from water.

Aminoacetophenone condenses with ethyl chloroformate, in anhydrous ethereal solution, to form *ethyl o-acetylphenylcarbamate*,



This melts at 91° and yields a little 2:4-dihydroxyquinoline (Friedländer and Weinberg, Abstr., 1883, 351) when it is boiled with dilute aqueous alcoholic sodium hydroxide, although for the most part it is decomposed into carbon dioxide and aminoacetophenone.

With phenylacetyl chloride in anhydrous ethereal solution, aminoacetophenone condenses to form *phenylacetyl-o*-aminoacetophenone,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2\text{Ph}$ . This melts at 79—80°; when boiled with dilute aqueous alcoholic sodium hydroxide, it is converted almost quantitatively into 2-hydroxy-3-phenyl-4-methylquinoline,



which melts at 275°, no isomeric 4-hydroxy-2-benzylquinoline being formed.

The other results described in the paper have been published already (Abstr., 1901, i, 751).

C. F. B.

**Condensations of Formaldehyde with Pyridine and Quinoline Derivatives.** By WILHELM KOENIGS (*Ber.*, 1901, **34**, 4322—4326. Compare *Abstr.*, 1899, i, 74, 389; 1900, i, 189).—The number of hydrogen atoms in a 2- or 4-derivative of pyridine or quinoline which can be replaced by methylol,  $\cdot\text{CH}_2\cdot\text{OH}$ , groups by the action of formaldehyde is always lessened by one when the 3- or 5-position contains as a substituent an alkyl group or a benzene nucleus. The same generalisation holds when both 3- and 5-positions are substituted. If, however, the 3- or 5-position is occupied by a carboxyl group, the introduction of methylol is facilitated rather than retarded.

Neither 2-methylpyridine nor 2-methylquinoline forms condensation products with paraldehyde, chloral, or benzaldehyde. J. J. S.

**Condensation of Formaldehyde with 2-Ethylquinoline and with 3-Methyl-2-ethylquinoline.** By WILHELM KOENIGS and EDUARD BISCHKOPF (*Ber.*, 1901, **34**, 4327—4330. Compare preceding abstract).—2-*α*-Dimethylolethylquinoline,  $\text{C}_9\text{NH}_6\cdot\text{CMe}(\text{CH}_2\cdot\text{OH})_2$ , is formed when 2-ethylquinoline is heated with excess of a solution of formaldehyde under pressure for 48 hours; it crystallises from petroleum in colourless needles melting at 95—96°; the *hydrochloride* crystallises in colourless needles melting at 178—179°; the *aurichloride* forms pale yellow granules, and the *mercurichloride* greyish-white flakes. 2-*α*-Methylolethyl-3-methylquinoline,  $\text{C}_{15}\text{H}_{15}\text{ON}$ , prepared from 3-methyl-2-ethylquinoline and formaldehyde, is a crystalline solid melting at 87—88°; the *platinichloride* crystallises in reddish-yellow needles melting and decomposing at 200—205°; the *mercurichloride* forms white crystals, the *aurichloride* pale yellow needles, and the *cadmioidide* pale yellow crystals melting and decomposing at 157—160°. Attempts to prepare 2-*α*-dimethylolethyl-3-methylquinoline failed. 3-Methylquinoline does not condense with aldehydes, and thus resembles  $\beta$ -picoline. K. J. P. O.

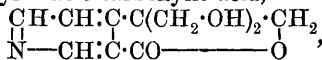
**Condensation of  $\beta$ -Methylquinaldine [2:3-Dimethylquinoline] and of 2-Methylquinoline-3-carboxylic Acid with Formaldehyde.** By WILHELM KOENIGS and FERDINAND STOCKHAUSEN (*Ber.*, 1901, **34**, 4330—4336. Compare preceding abstracts).—*Dimethylol-β-methylquinaldine* [2-dimethylolmethyl-3-methylquinoline],  $\text{C}_9\text{NH}_5\text{Me}\cdot\text{CH}(\text{CH}_2\cdot\text{OH})$ , is prepared by heating 2:3-dimethylquinoline with formaldehyde under pressure at 100°, and crystallises with  $\text{H}_2\text{O}$  in long needles melting at 85—86°; when anhydrous, it melts at 106—108°. The *platinichloride* crystallises in small, yellow needles melting and decomposing at 193°; the *hydrochloride* forms needles melting and decomposing at 200—201°; the *aurichloride*, yellow needles melting at 145°; the *cadmiiochloride* crystallises in white needles melting and decomposing at 207—209°, the *mercurichloride* in white needles melting at 136°; the *picrate* crystallises in long, yellow, silky needles melting at 170°. On oxidation with nitric acid, the base yields 3-methylquinoline-2-carboxylic acid (m. p. 144°).

The *lactone* of 2-trimethylolmethylquinoline-3-carboxylic acid,  $\text{C}_9\text{NH}_5\left\langle\begin{array}{c} \text{CO} \text{---} \text{O} \\ \text{C}(\text{CH}_2\cdot\text{OH})_2 \end{array}\right\rangle\text{CH}_2$ , is formed when 2-methylquinoline-3-

carboxylic acid is heated at 100° for many hours with great excess of formaldehyde under pressure, and crystallises from water with H<sub>2</sub>O in white needles melting at 167—168°; the *hydrochloride* crystallises in long, white needles melting and decomposing at 189—191°; the *platinichloride* crystallises, with 2H<sub>2</sub>O, in red needles, plates, or leaflets, which darken at 180° and finally melt and decompose at 216—217°; the *aurichloride* crystallises in long, thin, golden-yellow needles, melting and decomposing at 209—210°; the *picrate* forms tufts of yellow, lustrous needles, melting and decomposing at 142—143°. When oxidised with nitric acid, acridinic acid (Graebe and Caro, Abstr., 1880, 398) is obtained. The lactone is insoluble in sodium carbonate, but immediately dissolves in sodium or barium hydroxide; carbon dioxide reprecipitates the lactone from these solutions.

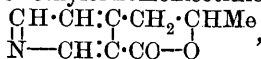
K. J. P. O.

Condensation Products of Homonicotinic Acid [4-Methylpyridinecarboxylic Acid] with Formaldehyde and Acetaldehyde. By WILHELM KOENIGS (*Ber.*, 1901, 34, 4336—4342. Compare preceding abstracts).—When homonicotinic acid is heated with formaldehyde solution under pressure at 100°, the lactone of 4-trimethylolmethylpyridine-3-carboxylic acid,

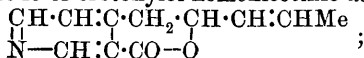


is formed; it crystallises from ethyl acetate in colourless needles melting at 148°; the *hydrochloride* is very soluble in water; the *aurichloride* crystallises in yellow, flattened needles or plates, the *platinichloride* in orange-red, four-sided plates melting and decomposing at 230°; the *picrate* crystallises in pale yellow needles or scales, which melt and decompose at 204°. A *monoacetyl* derivative is obtained by boiling the crude lactone with excess of acetic anhydride, and crystallises in colourless prisms which melt at 153—154°, and volatilise undecomposed. When heated with aqueous sodium hydroxide, an amorphous sodium salt is formed. Oxidising agents, especially nitric acid, convert the lactone into cinchomeronic acid.

When acetaldehyde (or paraldehyde) and homonicotinic acid are heated at 140—150° under pressure, two substances are formed which can be separated by fractional crystallisation of their picrates from water. From the more soluble picrate (m. p. 143°), the *platinichloride* of the lactone of ethylol-homonicotinic acid,



is obtained in reddish-yellow crystals, which darken at 240° but do not melt at 278°. From the less soluble picrate (m. p. 186°), a *platinichloride*, (C<sub>11</sub>H<sub>11</sub>O<sub>2</sub>N)<sub>2</sub>·H<sub>2</sub>PtCl<sub>6</sub>, is obtained in yellowish-red crystals melting and decomposing at 238°. The author believes the base to be the lactone of crotonylol-homonicotinic acid,



the base exhibits a blue fluorescence in solution in ethyl acetate; with

cadmium chloride, the hydrochloride of the base gives a double *salt* crystallising in yellow needles, melting and decomposing at 230—231°.

K. J. P. O.

**Acridine. II.** By ALBERT EDINGER and W. ARNOLD (*J. pr. Chem.*, 1901, [ii], 64, 471—492. Compare Abstr., 1901, i, 753).—When heated with phosphorus pentachloride and phosphorus oxychloride at 120—130°, 5-thioacridone yields 5-chloroacridine (m. p. 119°). With red phosphorus and bromine, 5-bromoacridine,  $C_{13}H_8NBr$ , is mainly obtained; it crystallises in brownish-yellow needles melting at 116°, and in the presence of acids is very readily converted into acridone; the *platinichloride* forms small, brown, quadratic crystals; the *picrate* crystallises in small, yellow needles melting at 212—213°; the *hydrochloride* forms needles decomposing at 238°, and the *sulphate* yellow needles decomposing at 170°.

5-Iodoacridine,  $C_{13}H_8NI$ , cannot be obtained by the action of phosphorus and iodine on thioacridone, but is prepared by the action of sodium iodide on 5-bromoacridine in the presence of alcohol; it crystallises in brownish-yellow needles melting at 169°; the *sulphate* crystallises in yellow needles; the *platinichloride* crystallises in brownish-yellow needles, and the *picrate* in lemon-yellow needles melting at 204°.

5-Benzoylthioacridol,  $C_{13}H_8NBzS$ , obtained by benzoylating thioacridone by the Schotten-Baumann method, crystallises in yellowish-green leaflets melting at 209°; the *picrate* crystallises in yellowish-green needles melting at 190°.

5-Benzylthioacridol,  $C_6H_4 \begin{array}{c} C(S \cdot CH_2Ph) \\ | \\ N \end{array} > C_6H_4$ , prepared by the

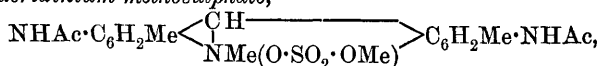
action of sodium ethoxide on a mixture of benzyl chloride and thioacridol dissolved in alcohol, crystallises in large, greenish-yellow needles melting at 109°; the *hydrochloride* and *nitrate* both crystallise in yellow leaflets, the former decomposing at 140—141°, the latter at 106—107°; the *platinichloride* is a brownish-yellow solid; the *picrate* crystallises in yellowish-brown, lustrous needles melting at 189—190°, whilst the *sulphate* forms yellowish-brown crystals melting and decomposing at 179—180°.

5-Methylthioacridol,  $C_{13}H_8N \cdot SMe$ , prepared by treating thioacridol and methyl iodide with sodium ethoxide in alcoholic solution, crystallises in greenish-yellow needles melting at 113—114°; the *hydrochloride* forms yellow needles melting at 198°; the *sulphate* melts at 156—157°; the *nitrate* melts and decomposes at 117—118°; the *platinichloride* is an ochre-yellow, crystalline powder, and the *picrate* forms lustrous needles melting at 205°. Alcoholic hydrochloric acid converts it into acridone and methylmercaptan. When thioacridol and methyl iodide are heated under pressure at 75—80°, the methyl ether just mentioned is formed; at 150°, a substance containing no sulphur, but much iodine, is obtained, which, with sodium carbonate, yields mainly acridone; at 250°, acridine hydriodide and iodine are produced.

A tetramitroacridone,  $C_{13}H_4ON(NO_2)_4$ , is formed when thioacridol is heated with concentrated nitric acid under pressure; it forms insoluble lemon-yellow crystals melting above 350°, and dissolves in alkalis with a cherry-red coloration.

K. J. P. O.

**Diaminoacridinium Compounds.** By FRITZ ULLMANN and A. MARIĆ (*Ber.*, 1901, **34**, 4307—4316. Compare Abstr., 1900, i, 689).—2:8-Diamino-3:7-dimethylacridine (D.R.-P. 52324) crystallises from aniline in yellow needles, dissolves in concentrated sulphuric acid to a yellowish-green solution with a blue-green fluorescence, but is not readily soluble in organic solvents. The hydrochloride,  $C_{15}H_{16}N_8Cl$ , forms a microcrystalline, red powder and is only sparingly soluble in alcohol; the platinichloride is an insoluble, orange powder, and the *diacetyl* derivative crystallises from aniline in yellow needles. When dissolved in nitrobenzene and treated with methyl sulphate, the diacetyl derivative is converted into 2:8-diacetyl-amino-3:7:10-*trimethylacridinium methosulphate*,

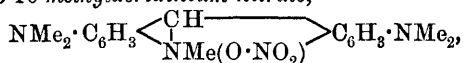


in the form of a reddish-yellow, crystalline precipitate readily soluble in water and also in concentrated sulphuric acid. The *chloride*,  $C_{20}H_{22}O_2N_3Cl$ , crystallises from alcohol, in which it is only sparingly soluble, in small, yellow needles. The *nitrate* is an orange-yellow, crystalline powder, and the *dichromate*,  $(C_{20}H_{22}O_2N_3)_2Cr_2O_7$ , separates from acetic acid in yellow crystals. Most of the salts are decomposed by ammonia, yielding a pale-coloured, crystalline substance insoluble in the usual solvents.

2:8-Diamino-3:7:10-*trimethylacridinium chloride*, obtained from the acetyl derivative by the action of hydrochloric acid, or from 2:8-diamino-3:7-dimethylacridine by transformation into the methosulphate and then into the chloride, crystallises in large, red needles which are readily soluble in water, yielding an orange-coloured solution with green fluorescence. The *nitrate* crystallises in red needles, sparingly soluble in alcohol, and the *dichromate* is an orange-red powder, insoluble in alcohol.

2-Nitro-4:4-tetramethyldiaminodiphenylmethane (D.R.-P. 79250) crystallises in brick-red needles melting at  $95^\circ$  and readily soluble in most organic solvents. On reduction with stannous chloride, it yields the 2-*amino*-derivative, which crystallises from a mixture of ether and light petroleum in pale rose-coloured plates melting at  $96^\circ$ . Dinitro-tetramethyldiaminodiphenylmethane (Pinnow, Abstr., 1901, i, 98) melts at  $195^\circ$  (corr.), not  $191.5^\circ$ .

Tetramethyldiaminoacridine (Biehringer, Abstr., 1897, i, 73) is readily alkylated by the action of methyl sulphate in toluene solution, and when the product is treated with nitric acid, it yields 2:8-*tetramethyldiamino-10-methylacridinium nitrate*,



in the form of long, dark-red needles with a steely lustre. It dissolves in concentrated sulphuric acid, but is practically insoluble in alcohol.

All these acridinium compounds dye tanned cotton with great readiness; the colours obtained are fast to alkalis, and vary from pure yellow to orange-red.

When the acridine derivatives are alkylated with halogen alkyls, they yield, even in neutral solutions, alkylated amino-derivatives and not acridinium compounds.



The dye known as patent phosphin (D.R.-P. 79703) contains no acridinium salt, but is an alkylated aminoacridine. J. J. S.

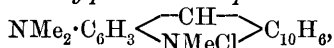
**3'-Dimethylamino-[Pheno]1:2-naphthacridine.** By FRITZ ULLMANN and A. MARIĆ (*Ber.*, 1901, **34**, 4317—4322. Compare Abstr., 1900, i, 360, 361).—2-Dimethylaminopheno-1:2-naphthacridine,

$\text{NMe}_2 \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{C}_{10}\text{H}_6$ , or its leuco-derivative may be obtained by

the action of  $\beta$ -naphthol on tetramethyltetra-aminodiphenylmethane or on the anhydroformaldehyde derivative of *m*-aminodimethylaniline, also by the action of dihydroxydinaphthylmethane on *m*-aminodimethylaniline and the action of  $\beta$ -naphthol on *m*-aminodimethylaniline and paraformaldehyde; the yields are good. It crystallises from a mixture of benzene and light petroleum in stellate groups of large, yellowish-red needles or in thick, quadratic plates melting at  $185.5^\circ$ , and dissolves in concentrated sulphuric acid and in alcohol, yielding fluorescent solutions. The *hydrochloride* forms dark-brown needles soluble in water or alcohol; the *nitrate* forms red needles sparingly soluble in water; the *dichromate* is insoluble in water, and the *picrate* crystallises in red plates insoluble in alcohol, ether, or benzene.

The *leuco*-compound,  $\text{C}_{19}\text{H}_{18}\text{N}_2$ , crystallises from benzene in plates melting at  $202-207^\circ$  and insoluble in alcohol or ether.

2-Dimethylamino-12-methylpheno-1:2-naphthacridinium chloride,



crystallises in red needles, soluble in water or alcohol to fluorescent solutions which do not change on the addition of ammonium or sodium hydroxide solutions. The *dichromate* is a red, crystalline powder insoluble in alcohol, but readily soluble in acetic acid. J. J. S.

**Naphthacridones and Naphthacridines.** By ERICH STROHBACH (*Ber.*, 1901, **34**, 4146—4158. Compare Möhlau, Abstr., 1896, i, 242).—Naphthacridone is produced by heating 2-hydroxy-3-naphthoic acid with  $\beta$ -naphthylamine at  $260-280^\circ$  for 10—12 hours; it is accompanied by smaller quantities of  $\beta\beta$ -dinaphthylamine, 2-hydroxy-3-naphtho- $\beta$ -naphthalide,  $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7$ , and traces of  $\beta$ -naphthylamino-3-naphthoic acid,  $\text{C}_{10}\text{H}_7 \cdot \text{NH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CO}_2\text{H}$ . When the heating is carried out in the presence of phosphorus oxychloride, the yield of the bye-products is increased. 2-Hydroxy-3-naphtho- $\beta$ -naphthalide is more conveniently prepared by heating a mixture of methyl 2-hydroxy-3-naphthoate and  $\beta$ -naphthylamine with phosphorus oxychloride at  $180-200^\circ$ ; it crystallises from pyridine or water in lustrous, yellowish-white leaflets and melts at  $243-244^\circ$ .  $\beta$ -Naphthylamino-3-naphthoic acid crystallises from alcohol or water in yellow needles and melts at  $222-225^\circ$ .

14-Ethyl- $\beta_1\beta_2\alpha_1'\beta_1'$ -naphthacridone,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{NEt} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{C}_{10}\text{H}_6$ , obtained by heating the potassium derivative of  $\beta_1\beta_2\alpha_1'\beta_1'$ -naphthacridone with excess of ethyl iodide at  $130-150^\circ$ , crystallises from acetone in lustrous, yellow needles melting at  $204.5-205^\circ$ . The ethyl compound dissolves in the ordinary organic solvents, its solutions having a green fluor-

escence. The solution of the substance in concentrated sulphuric acid has a reddish-orange colour, and develops a yellowish-green fluorescence on warming.

The unsymmetrical constitution is given to naphthacridone and its ethyl derivative, in view of the fact that it is the  $\alpha$ -hydrogen atom contiguous to the  $\beta$ -amino-group which is displaced in condensations with  $\beta$ -naphthylamine (compare Lellmann and Schmidt, Abstr., 1888, 289, and Morgan, Trans., 1900, 77, 814).

14-Iodo- $\beta_1\beta_2\alpha_1'\beta_1'$ -naphthacridine hydriodide,  $C_{10}H_6 \begin{smallmatrix} \text{NHI} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix} I C_{10}H_6$ ,

results from the action of hydriodic acid of sp. gr. 1.70 on  $\beta_1\beta_2\alpha_1'\beta_1'$ -naphthacridone at 160—180°; it is a reddish-orange, crystalline substance darkening on exposure to light, and decomposing at 180—190°. When heated with acetone or alcohol, it reverts to naphthacridone.

$\beta_1\beta_2\alpha_1'\beta_1'$ -Naphthacridine,  $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} C_{10}H_6$ , produced by heating a mixture of the corresponding acridone and zinc dust in a stream of hydrogen, dissolves in pyridine and less readily in the other organic solvents; it is, however, insoluble in water. The base melts at 205.5—206°; its solutions in all solvents except concentrated sulphuric acid have a yellowish-green fluorescence.

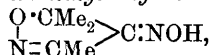
The preceding base is termed by the author " $\beta$ -naphthacridine," whilst Reed's isomeride melting at 216° (Abstr., 1886, 1037) is indicated by the index letter " $\alpha$ ."

G. T. M.

**Action of Nitrous and Nitric Acids on Mesityloxideoxime.** By CARL D. HARRIES (*Annalen*, 1901, 319, 230—256).—Mesitylnitrimine, the product of the action of nitrous acid on the stereoisomeric mesityloxideoximes (compare Abstr., 1898, i, 400, 568; 1899, i, 566), when reduced with zinc dust and water, yields trimethyldihydropyrazoline boiling at 63—64° under 23 mm. pressure (compare Curtius and Wirsing, Abstr., 1894, i, 248). This base is also obtained by reducing the hydrogen chloride compound of the nitrimine; the nitrimine may have one or other of the following formulæ,  $CH \begin{smallmatrix} \text{CMe} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{CMe}_2 \end{smallmatrix} \text{N} > \text{O}$

or  $\text{CMe}_2 \cdot \text{CH} \cdot \text{CMe} \cdot \text{N} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix}$ .

isoMesitylnitrimine (*ketotrimethyldihydroisooxazoleoxime*),



produced by heating mesitylnitrimine with water at 120°, crystallises from chloroform in white leaflets and melts at 156—157°; it has the properties of an oxime, forms a sodium derivative, does not reduce Fehling's solution until after hydrolysis with dilute sulphuric acid, and is not affected by bromine or by zinc dust and water. Its *acetyl* derivative crystallises from light petroleum or alcohol, and melts at 68—69°.

*Ketotrimethyldihydroisooxazole*,  $\begin{smallmatrix} \text{O} \cdot \text{CMe}_2 \\ \text{N} = \text{CMe} \end{smallmatrix} > \text{CO}$ , obtained by mixing

the oxime with cold concentrated nitric acid and heating the oily product,  $C_6H_9O_5N_3$ , either by itself or with acetic anhydride, is a colourless, refractive oil boiling at  $50-51^\circ$  under 16 mm., and at  $151^\circ$  at the ordinary pressure; it has a pleasant odour, and a sp. gr. 1.020 at  $27^\circ$ . On treatment with hydroxylamine, it regenerates *iso*-mesitylnitrimine and with phenylhydrazine, the *phenylhydrazone*,  $O \cdot CMe_2 \cdot N = CMe \cdot C : N \cdot NHPH$ , is obtained, which crystallises from alcohol or light petroleum in yellow needles melting at  $140-141^\circ$ .

*iso*Mesitylnitrimine, when boiled with dilute acids, is completely broken down, and nothing but a small amount of acetoxime is obtained.

*Mesitylgyloximeperoxide nitrite*,  $O \begin{smallmatrix} O-N \\ \diagup \quad \diagdown \\ N:CH \end{smallmatrix} C \cdot CH_2 \cdot CMe_2 \cdot O \cdot NO$ , produced by gently warming mesityloxideoxime in dilute nitric acid of sp. gr. 1.1, crystallises from methyl alcohol, acetone, glacial acetic acid, or acetic anhydride in golden-yellow leaflets or needles, and melts at  $128-129^\circ$ .

*α-Nitromesityl-β-anil*,  $NO_2 \cdot CH_2 \cdot C(NPh) \cdot CH : CMe_2$ , prepared by adding aniline to the preceding nitrite suspended in dry ether, crystallises from the ordinary organic solvents in yellow leaflets melting at  $84-85^\circ$ ; it yields *α*-nitromesityloxide,  $CMe_2 \cdot CH : CO \cdot CH_2 \cdot NO_2$ , and aniline on hydrolysis with dilute mineral acids, this product being a yellow oil boiling at  $95-96^\circ$  under 23 mm. pressure and having a sp. gr. 1.212 at  $27.3^\circ$ . The nitro-group in this compound is attached to a primary carbon atom, the substance giving a well-defined sodium derivative. The nitro-compound decolorises bromine, and when treated with semicarbazide and aniline gives rise to the semicarbazone and anil derivatives of nitroacetone respectively; the former of these crystallises in needles melting at  $163-164^\circ$ , and the latter, which is also obtained by the action of aniline on mesitylgyloximeperoxide nitrite in glacial acetic acid, crystallises from alcohol or light petroleum in amber-coloured needles or prisms sintering at  $80^\circ$  and melting at  $87^\circ$ . The anil derivative is quantitatively hydrolysed into nitroacetone by heating with 25 per cent. sulphuric acid.

The foregoing reactions constitute a ready method of preparing nitroacetone (compare Lucas, Abstr., 1900, i, 82), 100 grams of mesityloxide furnishing 35 grams of the product.

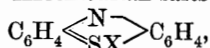
Nitroacetone boils at  $103-104^\circ$  under 24 mm., and at  $185-190^\circ$  under the ordinary pressure. When distilled in large quantities, it decomposes at  $165^\circ$  into acetic acid and a substance having an odour of prussic acid, probably cyanic acid.

The *sodium* derivative,  $COMe \cdot CH : NO_2Na$ , separates in colourless crystals, and the *silver* derivative in yellow needles. The nitro-compound neither reduces ammoniacal silver nitrate nor forms an oxide with nitrous acid; it yields acetylmethylnitrolic acid (compare Behrend and Tryller, Abstr., 1895, i, 201).

*α-Nitro-γ-benzylideneacetone*,  $CHPh : CH : CO \cdot CH_2 \cdot NO_2$ , produced by condensing nitroacetone with benzaldehyde in a 5 per cent. solution of sodium hydroxide, crystallises from alcohol in yellow plates, sinters at  $83^\circ$ , and melts at  $87-88^\circ$ .

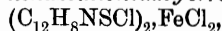
G. T. M.

**Azothionium Compounds.** By FRIEDRICH KEHRMANN (*Ber.*, 1901, **34**, 4170—4174).—Azothionium salts of the type



analogous to the azoxonium salts (compare Abstr., 1900, i, 61; 1901, i, 484; Werner, Abstr., 1901, i, 50) are obtained by oxidising thiodiphenylamine derivatives with acid oxidising agents.

[With V. VESELY.]—*Phenazothionium ferrochloride*,

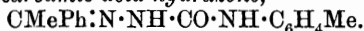


obtained by adding a cold alcoholic solution of thiodiphenylamine to ice-cold alcoholic ferric chloride, forms brownish-green crystals.

*Phenazothionium bromide*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{S} \text{Br} \end{array} \text{C}_6\text{H}_4$ , obtained by mixing cold alcoholic solutions of thiodiphenylamine and of bromine, is a coarsely crystalline, olive-green powder. *Phenazothionium picrate* is a greyish-green, sandy, crystalline powder. W. A. D.

**A New Reaction of Semicarbazones.** By WALTHER BORSCHÉ (*Ber.*, 1901, **34**, 4297—4302. Compare Kipping, Proc., 1900, 63; Young, *ibid.*, 73).—When salicylsemicarbazone is heated at 250—300°, it yields *o*-hydroxybenzylideneazine; when boiled with aniline for some time, the products are the same azine and *s*-diphenylcarbamide, or when the boiling is continued for only a short time, a third product, phenyl-*o*-hydroxybenzylidenesemicarbazone (Curtius and Hofmann, Abstr., 1896, i, 647), is also formed.

*Acetophenonesemicarbazone* crystallises in colourless plates melting and decomposing at 198—199°; when boiled with aniline, it yields *acetophenonephenylcarbamid acid hydrazone* melting at 187—188°. *Acetophenonesemicarbazone* and *o*-toluidine yield di-*o*-tolylcarbamide and *acetophenone-o-tolylcarbamid acid hydrazone*,



The latter crystallises from alcohol in long, colourless needles, melts at 211—212°, and is not readily converted into the corresponding azine. *Acetonesemicarbazone* and  $\beta$ -naphthylamine yield *acetone- $\beta$ -naphthylcarbamid acid hydrazone* in the form of pale red needles melting at 192—193° and di- $\beta$ -naphthylcarbamide. The reaction is best carried out in the presence of dimethylaniline.

Tertiary bases do not react with semicarbazones in the same manner as aniline. J. J. S.

**Pyridazines.** By ALFRED OPPENHEIM (*Ber.*, 1901, **34**, 4227—4234. Compare Abstr., 1899, i, 390).—Disubstituted pyridazines have been synthesised by the action of hydrazine on  $\gamma$ -ketonic acids of the formula  $\text{X}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHR}\cdot\text{CO}_2\text{H}$ .

*Benzoyldimethylmalonic acid*,  $\text{CH}_2\text{Bz}\cdot\text{CMe}(\text{CO}_2\text{H})_2$ , obtained when the sodium compound of ethyl isosuccinate suspended in ether is treated with bromoacetophenone, is a yellow, crystalline substance which melts at 145° with the evolution of carbon dioxide, yielding an acid which is identical with the  $\beta$ -benzoyl- $\alpha$ -methylpropionic acid obtained by Klobb (Abstr., 1900, i, 498) by the condensation of pyrotartaric anhydride with benzene.

$\beta$ -Benzoyl- $\alpha$ -methylpropionic acid condenses with hydrazine, forming

*3-phenyl-5-methylpyridazinone*,  $\text{NH} \begin{smallmatrix} \text{N} - \text{CPh} \\ \text{CO} \cdot \text{CHMe} \end{smallmatrix} \text{CH}_2$ , which crystallises in rhombohedra, melts at  $157.5^\circ$ , is soluble in most organic solvents except light petroleum, and when treated with bromine yields the corresponding *pyridazone*, which crystallises from alcohol in small, colourless needles and melts at  $189-190^\circ$ . On treating the latter with phosphorus oxychloride, it yields *6-chloro-3-phenyl-5-methylpyridazine*, which crystallises from alcohol in slender needles, and melts at  $141-142^\circ$ , and, when treated with hydriodic acid, yields *3-phenyl-5-methylpyridazine*, which crystallises in long, silky needles and melts at  $95^\circ$ ; the *hydriodide* of the latter crystallises in yellowish-brown needles, sinters at  $90^\circ$ , and is completely molten at  $140^\circ$ , and the *chromate* crystallises in slender, felted needles. The chloropyridazine, when treated with sodium ethoxide, yields *6-ethoxy-3-phenyl-5-methylpyridazine*, which crystallises in slender needles, melts at  $103-104^\circ$ , and forms an insoluble *aurichloride*, a *chromate*, and a *picrate* melting at  $150^\circ$ ; the analogous *6-methoxy*-compound crystallises from alcohol in slender, felted needles, and melts at  $60-61^\circ$ ; *6-anilino-3-phenyl-5-methylpyridazine*, obtained when the chloro-compound is treated with aniline, is a white, crystalline substance which melts at  $173-174^\circ$ , and forms an insoluble *chromate*.

R. H. P.

**Derivatives of Pyrimidine.** By WILLIAM O. EMERY (*Ber.*, 1901, 34, 4178—4181).—When dialuric acid is heated with phosphorus pentachloride, initially on the water-bath, and finally in a sealed tube for half an hour at  $120^\circ$ , it is converted into the same tetrachloropyrimidine as was formerly obtained in the same way from alloxan (Ciamician and Magnaghi, *Abstr.*, 1886, 226); the latter melts at a temperature slightly higher ( $70^\circ$ ) than formerly given ( $67-68^\circ$ ), and is not changed by distilling with zinc dust or by sodium amalgam. When heated with sodium iodide in alcoholic solution for 10 hours, it is converted into a mixture of *trichloroiodopyrimidine*,  $\text{C}_4\text{N}_2\text{Cl}_3\text{I}$ , and *dichlorodiiodopyrimidine*,  $\text{C}_4\text{N}_2\text{Cl}_2\text{I}_2$ ; these are separated on recrystallisation from methyl alcohol, the latter being obtained in needles melting at  $159^\circ$ , and the former in yellowish nodules melting at  $93-94^\circ$ .

*Tetrabromopyrimidine*,  $\text{C}_4\text{N}_2\text{Br}_4$ , obtained from dialuric acid and phosphorus pentabromide, is volatile with steam, and forms snow-white crystals melting at  $165-166^\circ$ .

When tetrachloropyrimidine is boiled with zinc dust and water for a long period, the whole of the halogen is removed and pyrimidine formed (compare Gabriel and Colman, *Abstr.*, 1899, i, 638).

W. A. D.

**Nitroprusside, Ferrocyanide, and Ferricyanide of Antipyrine.** By M. C. SCHUYTEN (*Chem. Centr.*, 1901, ii, 1362; from *Handel. van het vijfde Vlaamsch Natuur Geneeskundig Congres, Brugge*, 1901).—These antipyrine salts are readily prepared by processes of double decomposition. The *nitroprusside*,  $(\text{C}_{11}\text{H}_{12}\text{ON}_2)_2 \cdot \text{H}_2\text{Fe}(\text{NO})(\text{CN})_5 \cdot \text{H}_2\text{O}$ , is a pale brown, amorphous substance, melts at  $77-78^\circ$ , is soluble in water, and has an acid reaction. Aqueous solutions become blue on exposure to air and solution in acetone green. *Antipyrine ferrocyanide*,  
 $(\text{C}_{11}\text{H}_{12}\text{ON}_2)_2 \cdot \text{H}_4\text{Fe}(\text{CN})_6$ .

is a white substance. *Antipyrine ferricyanide*,  
 $(C_{11}H_{12}ON_2)_3H_3Fe(CN)_6$ ,  
 forms yellow, needle-shaped crystals, and is readily soluble in water.  
 E. W. W.

**Compounds of Antipyrine with Ferric Haloids.** By M. C. SCHUYTEN (*Chem. Centr.*, 1901, ii, 1362—1363; from *Handel van het vijfde Vlaamsch Natuur Geneeskundig Congres, Brugge*, 1901).—Antipyrine ferric chloride (Hasse's ferropyrine, *Pharm. Centr.-H.*, 36, 59),  $(C_{11}H_{12}ON_2)_3FeCl_3$ , prepared by mixing aqueous or ethereal solutions of ferric chloride and antipyrine, is an orange-yellow powder, which becomes brown at 150°, melts at 205°, and is readily soluble in water. The aqueous solution has an acid reaction, and when warmed gives a brown precipitate which partially redissolves on cooling. The action of many reagents on the aqueous solution of antipyrine ferric chloride is described in the original paper.

Antipyrine ferric bromide and antipyrine ferric iodide cannot be prepared by mixing the components or by double decomposition, and are doubtless unstable under ordinary conditions.  
 E. W. W.

**Synthesis of Uracil, Thymin, and Phenyluracil.** By EMIL FISCHER and GEORG ROEDER (*Ber.*, 1901, 34, 4129. Compare this vol., i, 124).—4-Phenyluracil, prepared by the authors from its hydro-compound, was first obtained by Warmington from ethyl benzoylacetate and carbamide (*Abstr.*, 1893, i, 369).

Weidel and Roithner had already obtained 4-methylhydrouracil in an impure form, and hydrouracil has been described under the name of  $\beta$ -lactylcarbamide by Lengfeld and Stieglitz (*Abstr.*, 1893, i, 632).

G. T. M.

**Benziminazoles.** By OTTO FISCHER and MORITZ RIGAUD (*Ber.*, 1901, 34, 4202—4209).—*s*-Dimethylphenylenediamine combines readily with aromatic aldehydes at the ordinary temperature with elimination of  $1H_2O$ ; the products are easily hydrolysed into their components, however, by dilute acids and alkalis. The compound,  $C_{15}H_{16}N_2$ , obtained from benzaldehyde, crystallises from methyl alcohol and melts at 102—103°; the derivative,  $C_{15}H_{16}ON_2$ , obtained from salicylaldehyde forms short, colourless prisms and melts at 155°.

[With W. KOPF.]—1-Phenylbenziminazole,  $C_{15}H_{10}N_2$ , obtained by boiling *o*-aminodiphenylamine with formic acid for several hours, crystallises from light petroleum in concentrically grouped needles and melts at 97°; the *platinichloride* forms reddish-yellow prisms or leaflets, the *mercurichloride* long, pike-shaped crystals, and the *picrate*, slender needles which change into prisms.

The *methiodide*,  $C_{14}H_{15}N_2I$ , crystallises from water in colourless leaflets, melts at 200°, and with warm aqueous sodium hydroxide yields the carbinol-base, 1-phenyl-3-methylbenziminazoleol,  $C_6H_4 \begin{smallmatrix} NMe \\ \diagup \\ NPh \end{smallmatrix} > CH \cdot OH$ ; this crystallises from dilute alcohol in colourless, flat prisms, melts at 168°, and is only very slowly hydrolysed by boiling aqueous sodium hydroxide. Ultimately, small quantities of an oily *o*-methylamino-

diphenylamine are obtained, the *hydrochloride* of which forms beautiful, colourless needles.

4:5-Diamino-*m*-xylene condenses readily with formic acid, giving 4:6-dimethylbenziminazole, which crystallises from chloroform, on adding light petroleum, in silvery leaflets, melts at 175°, and yields a crystalline *hydrochloride*, *platinichloride*, and *picrate*. When heated at 130°, with methyl iodide dissolved in methyl alcohol, it yields the 1:3:4:5-tetramethylbenziminazole methiodide,  $C_{11}H_{15}N_2I$ , which crystallises in white needles and melts at 278—279°; the derived carbinol base,  $C_6H_2Me_2 \begin{smallmatrix} <NMe> \\ <NMe> \end{smallmatrix} CH \cdot OH$ , crystallises from light petroleum in colourless, acutely truncated prisms, melts at 135°, and is not affected by boiling aqueous alkaline hydroxides.

1:4:6-Trimethylbenziminazole iodide is formed as an easily soluble substance along with the foregoing less soluble, higher methylated derivative, when the parent benziminazole is simply warmed with methyl alcoholic methyl iodide; with potassium hydroxide, it yields a *base* which crystallises from light petroleum in colourless prisms and melts at 70°; the *platinichloride* forms reddish-yellow needles.

*p*-Nitro-*m*-tolyl ethyl ether crystallises from light petroleum in colourless prisms, melts at 55° (Staedel and Kolb, Abstr., 1891, 186, give 51°), and when heated for 10 hours with alcoholic ethylamine, is converted quantitatively into *p*-nitro-*m*-ethyltoluidine, which crystallises from dilute alcohol in yellowish-red needles and melts at 60°. *m*-Ethyl-*o*-tolylenediamine, obtained by reduction of the nitro-compound with tin and hydrochloric acid, crystallises from light petroleum in long, colourless needles, melts at 59°, and on boiling with acetic acid yields Hübner's 2:6-dimethyl-1-ethylbenziminazole (compare O. Fischer and Schilling, Abstr., 1893, 283), which thus has the structure  $CMe \cdot CH \cdot C \cdot NEt \begin{smallmatrix} | \\ CH=CH \cdot C-N \end{smallmatrix} > CMe$ . The isomeric 2:5-dimethyl-1-ethylbenz-

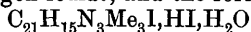
iminazole is shown to have the structure  $CMe \cdot CH \cdot C-N \begin{smallmatrix} | \\ CH=CH \cdot C \cdot NEt \end{smallmatrix} > CMe$  by its formation from 4-ethyl-3:4-tolylenediamine and glacial acetic acid; it crystallises from light petroleum in long, thin needles, is very hygroscopic and melts at 86—87°, not at 165—166° as stated by Schilling, whose compound probably contained, or consisted of, 3:4-diacetyl-4-ethyl-tolylenediamine, which melts, when pure, at 177°. The *platinichloride* of the  $\beta$ -azole crystallises in reddish-yellow prisms decomposing at 251°, the *aurichloride* in yellow tufts melting at 129—130°, and the *nitrate* melts at 133°; the *mercurichloride* melts at 190°, whilst the *picrate* forms small, bright yellow prisms, melts at 260—261°, and is very characteristic. The *picrate* of the  $\alpha$ -azole melts at 232—233°, and the *mercurichloride* at 149—150°.

On heating the hydrochloride of either the  $\alpha$ - or  $\beta$ -azole on the sand-bath, ethyl chloride is evolved, and the same ethenyl-3:4-tolylenediamine (m. p. 198°) is obtained in both cases; the latter is thus tautomeric according to von Pechmann's views. W. A. D.

**Aminolophine.** By JULIUS TROEGER (*J. pr. Chem.*, 1901, [ii], 64, 530—546).—*m*-Nitrolophine,  $\begin{smallmatrix} CPh \cdot NH \\ | \\ CPh-N \end{smallmatrix} > C \cdot C_6H_4 \cdot NO_2$ , produced to-

gether with benzilam from *m*-nitrobenzaldehyde and benzil in presence of ammonia, is a crystalline powder almost insoluble in the ordinary organic solvents, and does not melt at 295°.

*m*-Aminolophine,  $\begin{matrix} \text{CPh}\cdot\text{NH} \\ | \\ \text{CPh}-\text{N} \end{matrix} \Rightarrow \text{C}_6\text{H}_4\cdot\text{NH}_2$ , forms minute, thread-like crystals, becomes brown at about 280°, and blackens and melts at 290°; it gives a dirty-white precipitate with phosphotungstic acid, a red-brown precipitate with potassium bismuthiodide, and a white precipitate with potassium mercuric iodide, a dark yellow precipitate with potassium zinc iodide, a white precipitate with lead acetate, and a dark-brown, crystalline precipitate with iodine in potassium iodide; the *hydrochloride*,  $\text{C}_{21}\text{H}_{17}\text{N}_3\cdot 2\text{HCl}$ , separates in needles on adding concentrated hydrochloric acid to a solution of the base in the dilute acid; the *platinichloride*,  $(\text{C}_{21}\text{H}_{17}\text{N}_3)_2\cdot \text{H}_2\text{PtCl}_6$ , forms a pale flesh-coloured precipitate; the *nitrate*,  $\text{C}_{21}\text{H}_{17}\text{N}_3\cdot \text{HNO}_3$ , crystallises in needles; the *sulphate*, is only slightly soluble in water, and separates in clusters of crystals; the *picrate*,  $\text{C}_{21}\text{H}_{17}\text{N}_3\cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , forms brownish-yellow needles, and melts and decomposes at 200°; the *aurichloride* forms a brown precipitate. *m*-Aminolophine *tetraiodide*,  $\text{C}_{21}\text{H}_7\text{N}_3\text{HI}_4$ , forms brown needles, and decomposes when heated above 200°. The product of the action of methyl iodide on *m*-aminolophine appears to contain loosely combined hydrogen iodide, and the formula



is provisionally assigned to it.

*p*-Aminolophine crystallises in minute needles and becomes brown and decomposes gradually above 180°; the *hydrochloride*,  $\text{C}_{21}\text{H}_{17}\text{N}_3\cdot 2\text{HCl}$ , forms small, compact crystals; the *nitrate* forms white needles, the *platinichloride* is a dirty brown-yellow precipitate, and the *aurichloride* a dark brown precipitate.

*o*-Aminolophine is a white, crystalline substance; the *hydrochloride*,  $\text{C}_{21}\text{H}_{17}\text{N}_3\cdot 2\text{HCl}$ , forms minute, white needles.

T. M. L.

**Ketone Reactions of  $\gamma$ -Lutidone.** By PAVEL IW. PETRENKO-KRITSCHENKO and S. MOSSESCHWILI (*J. pr. Chem.*, 1901, [ii], 64, 496).—With phenylhydrazine,  $\gamma$ -lutidone yields a *hydrazone*,  $\text{C}_{13}\text{H}_{15}\text{N}_3$ , as crystals melting at 125°. With hydroxylamine, an oxime is not formed, but a crystalline substance,  $\text{C}_7\text{H}_{10}\text{O}_2\text{N}$ , which melts at 249°.

K. J. P. O.

**Partial Hydrolysis of Triaminomesitylene.** By FRANZ WENZEL (*Monatsh.*, 1901, 22, 983—985).—Triaminomesitylene trihydrochloride, when boiled with glacial acetic acid, yields the hydrochloride of *diaminohydroxymesitylene*; the base forms yellow needles, melts at 94—96°, and with acetic anhydride yields the *triacetyl* derivative which has been previously obtained in the endeavour to acetylise triaminomesitylene (*Abstr.*, 1898, i, 580).

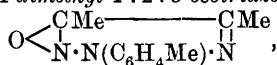
G. Y.

**Oxidation of Hydrazoximes. VI.** By GIACOMO PONZIO (*Gazzetta*, 1901, 31, ii, 413—416. Compare *Abstr.*, 1898, i, 386; 1899, i, 717, 827; 1900, i, 588; 1901, i, 169).—*Diacetyl-p-tolylhydrazoxime*,  $\text{NOH}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{N}_2\text{H}\cdot\text{C}_6\text{H}_4\text{Me}$ , prepared from isonitroso-



methyl ethyl ketone (diacetylmonoxime) and *p*-tolylhydrazine, crystallises from alcohol in yellowish prisms melting at 169°, and is soluble in chloroform, benzene, or ether.

4 : 5-Oxy-1-*p*-tolyl-3 : 4-dimethyl-1 : 2 : 5-osotriazole,



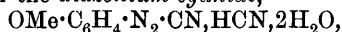
obtained by treating a chloroform solution of diacetyl-*p*-tolylhydrazoxime with yellow mercuric oxide under the conditions previously given (*loc. cit.*), crystallises from ether in pale yellow, shining prisms melting at 92—93°, and is soluble in water, light petroleum, alcohol, or chloroform. It is a mono-acid base, and has a weak basic reaction, its hydrochloride being instantly decomposed into its components in contact with water.

*Diacetyl-o-tolylhydrazoxime*,  $\text{C}_{11}\text{H}_{15}\text{ON}_3$ , separates from alcohol in faintly yellow, flattened prisms melting at 175° and is soluble in chloroform or ether.

*Diacetyl-β-naphthylhydrazoxime*,  $\text{C}_{14}\text{H}_{15}\text{ON}_3$ , crystallises from chloroform in rose-red laminae melting at 184°, and is soluble in acetone.

T. H. P.

**A Solid Diazonium Cyanide; Diazoiodides.** By HANS EULER and ARTHUR HANTZSCH (*Ber.*, 1901, 34, 4166—4169).—On adding concentrated potassium cyanide solution to a solution of anisole-diazonium chloride cooled to −80° and prevented from solidifying by the addition of alcohol, the *syn*-cyanide alone is formed, the low temperature apparently failing to influence the equilibrium between the *syn*-diazocyanide and diazonium cyanide; if, however, a solution of anisole-diazonium hydroxide, prepared by precipitating a solution of the bromide with moist silver oxide at 0°, be saturated with hydrogen cyanide and concentrated by freezing out and evaporating in a vacuum at 0—5°, crystals of the *diazonium cyanide*,



separate. With a dilution  $v_{100}$ , the mol. conductivity is 88, the salt thus electro-chemically resembling potassium cyanide; as it combines instantaneously with β-naphthol, a diazonium group is present. All three possible diazo-forms have thus been realised in the anisole series.

The solid diazo-haloids are to be regarded as solid solutions of colourless diazonium haloids and coloured *syn*-diazo-salts; the explosiveness is proportional to the depth of colour. The chlorides are colourless and not explosive, the bromides slightly, and the iodides strongly, coloured and explosive. The colour of the iodides depends on the temperature of formation, as shown in the case of the following salts precipitated from aqueous methyl alcoholic solutions by lithium iodide.

	At −60°.	At the ordinary temperature.
Anisole diazoiodide.....	Yellowish-white.	Golden-yellow.
<i>p</i> -Bromobenzenediazoiodide .....	Lemon-yellow.	Orange.
2 : 4-Dibromobenzenediazoiodide.	Golden-yellow.	Dark orange.
		W. A. D.

**New Method of Producing the Azobenzoic Acids.** By JOHANN MAIER (*Ber.*, 1901, 34, 4132—4134).—The three nitrobenzaldehydes, when heated with excess of aqueous sodium hydroxide solution (40° Be.), are first transformed into molecular proportions of nitrobenzoic acid and nitrobenzyl alcohol, but these products subsequently interact, yielding the corresponding azobenzoic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ .

G. T. M.

**The Influence of the Medium, especially of Inorganic Substances, on the Properties of Proteids.** By JOHANNES STARKE (*Zeit. Biol.*, 1901, 42, 187—227).—The influence of the medium (milieu) on the properties of proteids, especially that of heat coagulation, is discussed at length. Another point discussed is the influence of the medium on the solubilities and precipitability of acid and alkali-albumin. The conclusion arrived at is that there is no such influence exercised, but that the proteid molecule is as constant in its properties as other chemically defined substances.

W. D. H.

**Proteids. II.** By ADOLF JOLLES (*Monatsh.*, 1901, 22, 991—995. Compare Abstr., 1901, i, 490).—The author suggests that the greater the proportion of the total nitrogen of a proteid which, on oxidation, is separated as carbamide, the greater the value of the proteid as a food-stuff. The absorption of nitrogen by the human organism being taken as a guide, it is shown that casein (which yields 73 per cent. of its total nitrogen as carbamide) is utilised to a greater extent than is fibrin (which yields only 45 per cent.).

G. Y.

**The Aromatic Group of the Proteid Molecule.** By VIRGILIO DUCCESCHI (*Beitr. chem. Physiol. Path.*, 1901, 1, 339—346. Compare Fischer, Abstr., 1901, i, 745, 780).—When proteid is decomposed in hydrochloric acid solution by nitrous acid, cinnamic acid is a constant product. This points to the presence of a phenylalanine group in the proteid molecule.

W. D. H.

**The Aromatic Group in Gelatin.** By KARL SPIRO (*Beitr. chem. Physiol. Path.*, 1901, 1, 347—356).—Cinnamic acid is obtainable from gelatin as well as from various forms of proteid (see preceding abstract). Nencki has previously shown that phenylethylamine is a product of the putrefaction of gelatin.

W. D. H.

**Carbohydrate Groups in Albumin from Yolk of Egg.** By CARL NEUBERG (*Ber.*, 1901, 34, 3963—3967. Compare Blumenthal, Abstr., 1899, i, 465, 968).—The albumin from yolk of egg contains a group yielding glucosamine, since, when hydrolysed with hydrobromic acid and the products then oxidised with nitric acid, norisosccharic acid is formed. This is best isolated in the form of its cinchonine salt (this vol., i, 84). A salt isomeric with cinchonine norisosccharate is also formed. This is more readily soluble in alcohol, burns brown at 190°, decomposes at 230°, and has  $[\alpha]_D +150^\circ$ ; it is probably identical with *cinchonine d-saccharate*. *Quinine d-saccharate* melts at 174°, and closely resembles the cinchonine salt.

J. J. S.

**Serum-albumin of Ox Blood.** By A. HOUGARDY (*Trav. du lab. de L. Fredericq, Liège*, 1901, 6, 213—223; from *Arch. de Biol.*, 18).—According to Halliburton, the albumin of ox blood can be differentiated into two fractions by heat coagulation. The main fact is confirmed, but the author doubts whether this is sufficient proof of two different proteids. No other difference between the proteids is alleged to exist. Moreover, a single and total coagulation is obtainable at 65° if that temperature is maintained for 5 or 6 hours. W. D. H.

**Serum-globulin.** By PROSPER VAN DE KERCKHOF (*Trav. du lab. de L. Fredericq, Liège*, 1901, 6, 21—25; from *Arch. de Biol.*, 15, 640).—The serum-globulin of mammalian blood can be separated by fractional heat coagulation into three (in the dog into four) parts. No other differences are shown to demonstrate that these are separate proteids. No reference is made to recent work, which has shown that serum-globulin can be differentiated by dialysis into euglobulin and pseudoglobulin. W. D. H.

**Proteid Chemistry. Part I. A hitherto undescribed Product of Tryptic Digestion.** By F. GOWLAND HOPKINS and SYDNEY W. COLE (*J. Physiol.*, 1901, 27, 418—428).—The Adamkiewicz reaction depends on the presence of glyoxylic acid in the acetic acid used. During tryptic digestion, a crystalline product is produced which gives the reaction in a typical manner. The substance has the formula  $C_{11}H_{12}O_2N_2$ ; it yields skatole and indole when heated, and gives the pine-splinter reaction directly. The formula corresponds either with an indoleaminopropionic acid, or a scatoleaminoacetic acid, but this requires further investigation. The substance yields also a red derivative with bromine, and is in fact the hitherto unisolated tryptophan. W. D. H.

**Amounts of Hexone Bases obtained from Vegetable Proteids.** By ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1901, 33, 547—573. Compare Kossel and Kutscher, *Abstr.*, 1901, i, 107).—The yields of histidine, arginine, and lysine obtained by the action of hydrochloric acid on the proteids from the following seeds, have been determined:—*Picea excelsa*, *Pinus silvestris*, *P. maritima*, *Cucurbita Pepo*. Conglutin from the seeds of *Lupinus luteus* and other lupins, legumin from *Pisum sativum*, and edestin have also been hydrolysed and the percentages of bases determined. Except in the case of legumin, the amount of arginine is much greater than that of histidine or lysine, and is at a maximum in the proteid from *Pinus silvestris* and *P. maritima* and in edestin.

The histidine was estimated as its hydrochloride,  $C_6H_9O_2N_3.HCl.H_2O$ ; the arginine as the copper derivative,  $(C_6H_{14}O_2N_4)_2.Cu(NO_3)_2.3H_2O$ , and the lysine as its platinumchloride,  $C_6H_{14}O_2N_2.H_2PtCl_6$ .

The sum of the percentage of nitrogen present (1) as ammonia, (2) as hexone bases, is always far short of the total percentage of nitrogen present in the phosphotungstic acid precipitate. One source of loss lies in the retention of a certain amount of nitrogen compounds in the precipitate obtained on treating the phosphotungstic acid precipitate with baryta water.

If it is assumed that the amount of arginine produced by the hydrolysis of conglutin with acid is the same as is produced by the action of enzymes on the proteids of the seeds of *Lupinus luteus* during germination, then this amount is greater than that which has been actually found in the germinating plant. J. J. S.

**Caseinogen and its Salts.** By W. A. OSBORNE (*J. Physiol.*, 1901, 27, 398—406).—Caseinogen is an insoluble acid which forms soluble salts not only with potassium, sodium, and calcium, but also with other metallic and organic bases. The calcium salt is the chief proteid ingredient of milk; the ammonium salt is sold as eucasin, the sodium salt as nutrose and plasmon. All the salts are precipitated unchanged by half saturation with ammonium sulphate, full saturation with magnesium sulphate, or excess of alcohol. They liberate free caseinogen on treatment with an acid. They may be divided into two chief groups. Group I contains the calcium, magnesium, barium, and strontium salts; these are precipitated by any finely divided, insoluble substance, and will not pass through the pores of a clay filter. Their solutions are markedly opalescent; they become turbid on warming to 35—45°; this turbidity disappears on cooling. On prolonged heating, they form a film or 'skin' on the surface. They react with the rennin ferment. The caseinogenates of caffeine, strychnine, and other alkaloids belong to this group also, although they do not appear to react with rennin.

Group II contains the salts of potassium, sodium, and ammonium. These are not precipitated by finely divided substances, pass easily through a clay filter, form comparatively clear solutions, do not show the reversible change on warming, do not react with rennin, and no surface film is formed on warming. Lithium caseinogenate belongs to the same group, although it shows a faint turbidity on warming.

Calcium caseinogenate + potassium oxalate gives rise to calcium oxalate + potassium caseinogenate. Potassium caseinogenate + calcium chloride gives rise to calcium caseinogenate + potassium chloride. Certain caseinogenates show hydrolytic dissociation in a marked degree; this increases on warming, and explains the occurrence of the turbidity previously referred to. W. D. H.

**A Derivative of Casein containing Sulphur and Chlorine.** By THEODOR PANZER (*Zeit. physiol. Chem.*, 1901, 33, 595—608).—When casein is treated with hydrochloric acid and potassium chlorate, freed from excess of chlorine, treated with hydrogen sulphide, air dried, and then extracted for a month with carbon disulphide, the residue is a derivative of casein containing chlorine and sulphur. Its composition is C, 43.14; H, 5.10; N, 10.08; S, 8.86; P, 0.42; Cl, 8.36, and O, 24.04 per cent. It has decided acid properties, yielding *potassium*, *copper*, and *silver* compounds. It dissolves in dilute alkalis, alkali carbonate solutions, also in glacial acetic acid, or in alcohol containing acetic acid, and gives none of the usual proteid reactions. Part of the sulphur is removed on boiling with alkali, and the compound is completely decomposed when boiled with hydrochloric acid. J. J. S.

**Separation of Proteoses by Metallic Salts.** By ZDENKO ČERNÝ (*Pflüger's Archiv*, 1901, 87, 614—633).—The properties of

proteoses precipitated by various salts of heavy metals (silver, copper, uranium) are described and compared. The differences observed are believed to be due to the great lability of these substances, and the conclusion is drawn that the different known proteoses as separated by fractional precipitation with neutral salts do not really represent different substances present in the mixture. W. D. H.

**Mucin and Mucoids.** By FRIEDRICH MÜLLER (*Zeit. Biol.*, 1901, 42, 468—564).—A lengthy account of several mucins and mucoids. The question to which most attention is directed is the nature of the carbohydrate radicle, the so-called 'animal gum.' It is regarded as probable that it is an acetyl derivative of glucosamine. W. D. H.

**Crystallised Cyanohæmoglobin.** By RICHARD VON ZEYNEK (*Zeit. physiol. Chem.*, 1901, 33, 426—450. Compare Abstr., 1900, i, 318).—Crystallised methæmoglobin (Abstr., 1900, i, 196) dissolves in 0·5 per cent. hydrocyanic acid, yielding a reddish solution resembling oxyhæmoglobin and having a characteristic, broad absorption band in the green part of the spectrum. When diluted and mixed with alcohol at  $-10^{\circ}$ , microscopic crystals are obtained; as a rule, these have the shape of long prisms terminated by pyramids, but occasionally are rhomboid in shape. The same compound is obtained by the addition of potassium cyanide to alkaline methæmoglobin solution. It is stable, and may be heated at  $40^{\circ}$  in a stream of an indifferent gas, or its solution may be boiled at  $40^{\circ}$  under reduced pressure, without loss of hydrogen cyanide. When heated at  $105-110^{\circ}$  in a current of dry hydrogen, it loses water and a small amount of hydrogen cyanide; the same gas is evolved when it is boiled with water or acids under atmospheric pressure.

The compound contains 0·158 per cent. of cyanogen, a result which indicates the presence of only one cyanogen group in the molecule (mol. wt. of hæmoglobin = 16669).

The crystals are not affected by light, and bacteria cause only slow putrefaction. Treatment with hydrogen sulphide transforms the cyanogen derivative into hæmoglobin.

Back's (*Skand. Arch. Physiol.*, 6, 299) photomethæmoglobin appears to be identical with cyanohæmoglobin [this has been shown by Haldane, Abstr., 1900, i, 318] and is produced by the action of hydrogen cyanide liberated by the action of sunlight on potassium ferriocyanide.

Reduced hæmoglobin does not combine with hydrogen cyanide, but oxyhæmoglobin reacts with hydrocyanic acid solution at  $40^{\circ}$ , yielding the same cyanohæmoglobin. J. J. S.

**Action of Sunlight on Enzymes.** By OSKAR EMMERLING (*Ber.*, 1901, 34, 3811—3814).—The action of sunlight on 1 per cent. solutions of the following enzymes: invertase, yeast-maltase, maize-glucase, lactase, emulsin, and diastase, has been studied. The solutions were exposed for 6 hours and their fermenting properties then tested. With the exception of yeast-maltase, the enzymes suffered but very little deterioration owing to this exposure. Toxins, on the other hand, appear to be very susceptible to light. J. J. S.

**The Action of Enzymes on each other.** By AUGUSTIN WRÓBLEWSKI, B. BEDNARSKI and M. WOJCZYŃSKI (*Beitr. chem. Physiol. Path.*, 1901, 1, 289—303).—Pepsin destroys trypsin and hastens the destructive influence of acids; trypsin weakens the action of pepsin, especially in the presence of alkalis; pepsin has no action on rennet; pepsin, trypsin, and diastase have no action on invertin; trypsin and invertin have no action on, but pepsin slightly lessens the action of, diastase; pepsin and trypsin have no action on emulsin. Emulsin is completely 'salted out' by ammonium sulphate, and so differs from invertin. The statement of E. Fischer that emulsin hydrolyses lactose is confirmed. Zymase of yeast is rapidly destroyed by the proteolytic enzyme of the yeast cells.  
W. D. H.

**Tyrosinase.** By C. GESSARD (*Ann. Inst. Pasteur*, 1901, 15, 593—614. Compare Abstr., 1900, i, 468).—A further study of the colour changes induced by tyrosinase in tyrosine solutions containing various metallic salts shows that the compounds of iron (ferrous sulphate and lactate and ferric chloride) have a specific action, causing the development of a green coloration which changes to blue before the production of the bluish-black precipitate already noticed. This reaction takes place even when the solution has acquired the rose coloration produced in the presence of other metallic salts. Zinc salts, the lactate, for example, give rise to the blue coloration without the production of the intermediate green stage.

The time required for the development of the rose coloration increases very rapidly as the tyrosinase extract is diluted. When the extract is maintained at 65°, the chromogenic property diminishes, until after 30 minutes the tyrosinase is almost wholly destroyed.

Although the metallic salts promote the coagulation of the black precipitate, they hinder the development of the initial coloration, the retardation being proportional to the amount of salt introduced. The neutral salts produce a retardation varying from 23 minutes to 9 days, whilst the addition of an alkali carbonate prevents the development of the coloration for a period of 17 days. Albumin from the egg of the fowl also produces a very notable retardation. The serum of different animals (calf, sheep, pig, horse, mare, and rabbit) exhibits this inhibitive action, but to a less extent; calf serum has the greatest effect, whilst that of the rabbit is least efficacious. The inhibitive action of the rabbit serum is, however, very appreciably increased by repeatedly injecting the animal with an aqueous extract of tyrosinase.  
G. T. M.

**Synthetical Action of Yeast Maltase.** By OSKAR EMMERLING (*Ber.*, 1901, 34, 3810—3811).—A small amount of amygdalin is obtained when a mixture of Fischer's mandelonitrile glucoside (Abstr., 1895, i, 554) and pure dextrose is left in contact with a solution of yeast maltase (Abstr., 1901, i, 258) in sealed tubes for 3 months at 35°.  
J. J. S.

## Organic Chemistry.

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**Galician Petroleum. I. Nitration of the *iso*Hexane Fraction.** By ROMAN ZALOZIECKI and G. FRASCH (*Ber.*, 1902, **35**, 386—391).—By repeated fractionation of Galician petroleum, 42 fractions were obtained between 16° and 101°. The 10 fractions from 45° to 65°, which contain the hexanes, were each nitrated with a mixture of one part of nitric acid of sp. gr. 1·404 and three parts of sulphuric acid of sp. gr. 1·84. The crystalline products thus produced were fractionally crystallised from alcohol and yielded (i) a substance crystallising in long, yellow needles, melting at 89·5° (N = 19·38 per cent.), (ii) a much smaller quantity of a substance crystallising in small needles melting at 67° (N = 19·09 per cent.), and very small quantities of two other substances crystallising in needles and melting respectively at 65° and 61°. The authors conclude that these nitro-compounds are tertiary trinitrohexanes.  
K. J. P. O.

**Action of Oxidising Agents on Acetylene.** By A. BASCHIERI (*Gazzetta*, 1901, **31**, ii, 461—472).—The portion of this paper referring to the action of fuming nitric acid has already appeared (*Abstr.*, 1900 i, 534).

In either alkaline or acid solution, potassium permanganate oxidises acetylene to carbon dioxide and formic and oxalic acids. With chromic acid, no action takes place, even with very concentrated hot solutions.  
T. H. P.

**Preparation of Bromoform by Electrolysis.** By PAUL COUGHLIN (*Amer. Chem. J.*, 1902, **27**, 63—68).—In the electrolytic production of bromoform from acetone and an alkaline solution of potassium bromide, a better yield is obtained by using sodium carbonate than with sodium hydroxide. The optimum temperature is about 25°, and the current density has a considerable influence on the yield. Too much potassium bromide should not be used and the carbonate should be added only gradually. The yield decreases as excess of acetone is employed. When alcohol was used in place of acetone, only a small amount of bromoform could be obtained.  
J. McC.

**Transformation of Nitroparaffins.** By EUGEN BAMBERGER and ERNST RÜST (*Ber.*, 1902, **35**, 45—53).—The authors point out that not only may nitroparaffins,  $R \cdot CH_2 \cdot NO_2$ , be transformed into *isonitroparaffins*,  $R \cdot CH \cdot NO \cdot OH$ , which are recognised as existing in the salts of the nitroparaffins (Michael, Nef, Hantzsch, Holleman, &c.), but also into hydroxamic acids,  $R \cdot C(OH) \cdot NOH$ , and possibly into nitroso-alcohols,  $R \cdot CH(OH) \cdot NO$ . The decomposition of nitroparaffins into fatty acids and hydroxylamine (Victor Meyer, *Ber.*, 1875, **8**, 29) would then be expressed thus:  $R \cdot CH_2 \cdot NO_2 \rightarrow R \cdot C(OH) \cdot NOH; + H_2O \rightarrow R \cdot CO_2H$

+  $\text{NH}_2\cdot\text{OH}$ ; it is possible that the *isonitro*-compound is an intermediate stage between the nitroparaffin and the hydroxamic acid.

Acethydroxamic acid was obtained in very small quantity by acidifying with hydrochloric acid an alkaline solution of *isonitro*-ethane; after removing the hydrochloric acid with potassium acetate, copper acethydroxamate separated on addition of copper acetate. By a similar method, valerohydroxamic and benzhydroxamic acids were obtained from alkaline solutions of *isonitropentane* and *isophenyl*-nitromethane. From *iso-m*-xylylnitromethane, the hydroxamic acid was not isolated, although the solution gave the characteristic ferric chloride reaction of these acids.

Phenylnitromethane and *o*- and *p*-nitrophenylnitromethane, when treated with sulphuric acid of a certain strength, are converted into the corresponding hydroxamic acids; in the case of the two former nitro-compounds, the hydroxamic acid was only recognised by the ferric chloride reaction; from *p*-nitrophenylnitromethane, *p*-nitrobenzhydroxamic acid (m. p. 176—177°) was isolated. K. J. P. O.

**Action of Zinc Ethyl on Nitro- and Nitroso-compounds.** By ARTHUR LACHMAN (*J. Amer. Chem. Soc.*, 1901, 23, 897—902. Compare Dunstan and Goulding, *Trans.*, 1901, 79, 641—643).—The conclusions arrived at by the author based on the incorrect supposition that triethylamine oxide is formed by the action of zinc ethyl on nitroethane are withdrawn. The mechanism of the action of zinc alkyls on nitro- and nitroso-compounds is discussed, particularly with reference to the work of Bewad (*Abstr.*, 1900, i, 629). E. G.

**Action of Organo-magnesium Compounds on Trioxymethylene. Synthesis of Primary Alcohols.** By VICTOR GRIGNARD and L. TISSIER (*Compt. rend.*, 1902, 134, 107—108).—Trioxymethylene is gradually attacked when boiled with ethereal solutions of organo-magnesium compounds, and the reaction can be utilised as a general method for the preparation of primary alcohols in both the fatty and aromatic series, the yield in a given series being as a rule somewhat higher the lower the molecular weight of the alcohol. The author has prepared propyl alcohol from magnesium ethyl bromide; butyl alcohol from magnesium propyl bromide; *isohexyl* alcohol from magnesium *isoamyl* bromide; benzyl alcohol from magnesium benzyl bromide, and  $\alpha$ -naphthylmethanol from magnesium  $\alpha$ -naphthyl bromide. *isoHexyl* alcohol boils at 147—148° under 753 mm. pressure, and has a sp. gr. 0.8243 at 0°. It yields an acetate which boils at 159° under 755 mm. pressure, the odours of the acetate and the alcohol being very similar to those of the corresponding amyl compounds.

C. H. B.

**Supposed Preparation of Acetol [Acetylcarbinol].** By G. B. SIMONCINI (*Gazzetta*, 1901, 31, ii, 496—501).—The supposed formation of acetylcarbinol by the action of moist silver oxide on monobromoacetone is a more complex reaction than was assumed by Emmerling and Wagner (*Abstr.*, 1880, 867). The author has been unable to isolate any trace of the alcohol in this way, but in all



cases obtained difficultly separable mixtures of reducing oils of an aldehydic nature. These substances are probably polymerised formaldehydes and acetaldehydes, the formation of which is readily explicable by the ready oxidisability of acetylcarbinol; the latter compound, if formed in the reaction, undergoes instant oxidation under the action of silver oxide. T. H. P.

**Studies on Neutralisation. Colorimetric Titrations of Acids and Bases having Complex Functions.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1901, [vii], 25, 53—59).—A detailed account of work already published (compare Abstr., 1901, i, 497).

G. T. M.

**Preparation and Properties of Iminodithiocarbonic Esters.** By MARCEL DELÉPINE (*Compt. rend.*, 1902, 134, 108—110).—To prepare the iminodithiocarbonic esters (Abstr., 1901, i, 518), an alkyl iodide (2 mols.) is added to an alcoholic solution of a primary amine (2 mols.) previously mixed gradually with carbon disulphide (1 mol.). After some time, the liquid is diluted with four or five times its volume of water, and extracted with two or three successive small quantities of ether, which removes unaltered alkyl iodide, thiocyanates, and thiocarbimides and other bye-products. The alcoholic solution is then mixed with sodium hydroxide, which liberates the iminodithiocarbonic ester. The chief reaction is  $\text{RNH}\cdot\text{CS}\cdot\text{SNH}_3\text{R} + 2\text{R}'\text{I} = \text{RN}\cdot\text{C}(\text{SR}')_2 + \text{RNH}_3\text{I}$ , and the subsidiary reactions (a)  $\text{RNH}\cdot\text{CS}\cdot\text{SNH}_3\text{R} + \text{R}'\text{I} = \text{RNH}\cdot\text{CS}\cdot\text{SR}' + \text{RNH}_3\text{I}$ , (b)  $\text{RNH}\cdot\text{CS}\cdot\text{SR}' = \text{RN}\cdot\text{C}:\text{S} + \text{SHR}'$ , (c)  $\text{SHR}' + 2\text{R}'\text{I} = \text{SR}'_2\text{I} + \text{HI}$ .

The iminodithiocarbonic esters have a strong, peculiar odour, and are very mobile, refractive liquids, the lower members of the series being colourless, whilst the higher members have a yellowish tint. The boiling point increases but the sp. gr. decreases as the molecular weight rises, isomerides having, as a rule, the same boiling point and sp. gr., whilst a diminution in the proportion of hydrogen raises the sp. gr. The substitution of  $(\text{SEt})_2$  for  $(\text{SMe})_2$  raises the boiling point about  $20^\circ$ . The coefficient of expansion is about 0.00085 between  $0^\circ$  and  $20^\circ$ . The esters are soluble in acids but reprecipitated by alkalis, and are neutral to litmus and phenolphthalein but monobasic to methyl orange. All the platinichlorides and most of the picrates, mercurichlorides, and mercuri-iodides are crystallisable.

Constitution.	Sp. gr. $0^\circ/4^\circ$ .	Boiling point.	Melting point of platinichloride.
$\text{NMe}\cdot\text{C}(\text{SMe})_2$ .....	1.13827	$192^\circ$	$180^\circ$
$\text{NEt}\cdot\text{C}(\text{SMe})_2$ .....	1.08477	201	150
$\text{NMe}\cdot\text{C}(\text{SEt})_2$ ...	1.0594	215	161
$\text{NPr}\cdot\text{C}(\text{SMe})_2$ .....	1.0597	219	151
$\text{C}_3\text{H}_5\cdot\text{N}\cdot\text{C}(\text{SMe})_2$ .....	1.10093	220—222	145
$\text{NEt}\cdot\text{C}(\text{SEt})_2$ .....	1.02905	223—224	133
$\text{C}_4\text{H}_9\cdot\text{N}\cdot\text{C}(\text{SMe})_2$ .....	1.0262	225	132
$\text{C}_5\text{H}_{11}\cdot\text{N}\cdot\text{C}(\text{SMe})_2$ .....	1.0137	242—245	146
$\text{C}_5\text{H}_{11}\cdot\text{N}\cdot\text{C}(\text{SEt})_2$ .....	0.97906	260	123
$\text{C}_7\text{H}_7\cdot\text{N}\cdot\text{C}(\text{SMe})_2$ .....	1.1610 (?)	210—220 (60 mm.)	165

Determinations with the crystallised hydriodide,  $C_4H_9 \cdot NS_2, HI$ , gave the following results :

Heat of dissolution.  $-7.45$  Cal.

$C_4H_9NS_2, HI$ , diss. +  $KOH$  diss. =  $C_4H_9NS_2$ , liq. +  $KI$ , diss. develops +  $4.5$  Cal.

$C_4H_9NS_2$  liq. +  $HI$  diss. =  $C_4H_9NS_2, HI$  diss. develops +  $9.2$  Cal.

$C_4H_9NS_2$  liq. +  $HI$  gas =  $C_4H_9NS_2, HI$  cryst. develops +  $36.2$  Cal.

C. H. B.

**Brownish-black Substance obtained by the Action of Zinc Chloride on Acetic Anhydride.** By CARLO MONTANARI (*Gazzetta*, 1901, 31, ii, 479—496).—By the action of fused zinc chloride on acetic anhydride, Bauer (*Jahresber. Fortschr. Chem.*, 1861, 438) obtained a brown substance to which he assigned the composition  $(C_4H_2O)_x$ . The author's attempts to prepare this compound have been unsuccessful, substances always being obtained containing a less amount of carbon than required for the formula given above. The author has prepared bromo-derivatives of some of the products obtained by him, and has examined the cryoscopic behaviour of both the original substances and of their bromo-compounds, but has arrived at no conclusion as to their nature.

T. H. P.

**Condensation Product of Butyric Acid.** By GIACOMO ALBO (*Gazzetta*, 1901, 31, ii, 473—478).—On keeping a fraction of high boiling point ( $158-160^\circ$ ) of pure butyric acid for a long time, during part of which it was exposed to direct sunlight, it became transformed into a white, mucilaginous mass, which, after being thoroughly washed with ether and drying, was found to be an amorphous acid of the composition  $C_{13}H_{22}O_8$ . It is soluble in alcohol, alkali solutions, and sulphuric acid, and to a slight extent in water, and decomposes without melting at a temperature higher than  $220^\circ$ . When exposed to the air, the outer layers of the powder become vitreous and transparent. The silver salt,  $C_{13}H_{19}O_8Ag_3$ , is obtained as a flocculent, white precipitate, which is soluble in ammonia solution and quickly blackens on exposure to light. The copper salt,  $(C_{13}H_{19}O_8)_2Cu_3$ , forms a characteristic, pale blue, flocculent precipitate, soluble in ammonia. The barium salt is a white precipitate. Titration of the acid with potassium hydroxide yields the normal molecular weight for a tribasic acid. Attempts at esterification have not yet been successful. The author regards the acid as a polymeride of a compound of the simple formula given above.

T. H. P.

**Halogen Derivatives of the Aliphatic Acids.** By PAUL C. FREEB (*Annalen*, 1901, 319, 345—357).—A theoretical paper bearing on the following communications in which the influence exerted by the stereoisomerism and orientation of the halogen and carboxyl radicles in the halogen derivatives of aliphatic acids on the physical and chemical properties (electrical conductivity, esterification, hydrolysis, and lactone formation) of these compounds is discussed at considerable length.

G. T. M.

**Preparation of the Halogen Derivatives of Butyric and the  $\delta$ -Halogen Derivatives of Valeric Acids.** By A. M. CLOVES (*Annalen*, 1902, 319, 357—368).— $\alpha$ -Chlorobutyric acid is most easily obtained in

a pure state by chlorinating ethyl ethylmalonate with the theoretical amount of chlorine, distilling the product in a vacuum, hydrolysing the distillate with alcoholic potassium hydroxide at  $-10^{\circ}$ , and finally heating the chloroethylmalonic acid at  $140-150^{\circ}$ ; it is a colourless, highly refractive liquid boiling at  $101.25^{\circ}$  under 15 mm. pressure.  $\beta$ -Chlorobutyric acid results from the addition of hydrogen chloride to crotonic acid; there is no tendency to form the  $\alpha$ -isomeride in this reaction; the acid boils at  $98.5-99.5^{\circ}$  under 12 mm. pressure.  $\gamma$ -Chlorobutyric acid, prepared by hydrolysing  $\gamma$ -chlorobutyronitrile with boiling concentrated hydrochloric acid, heating the product at  $170-220^{\circ}$ , and treating the  $\gamma$ -butyrolactone so obtained with hydrogen chloride at  $-10^{\circ}$ , melts at  $16^{\circ}$ , and boils with slight decomposition at  $115-115.5^{\circ}$  under 13 mm. pressure.

This addition of hydrogen chloride is a reversible action and the formation of the chloro-derivative takes place very slowly; the velocity of the direct action is much greater in the case of the production of the corresponding bromo- and iodo-compounds.  $\delta$ -Iodovaleric acid is readily prepared by heating  $\delta$ -phenoxyvaleric acid with fuming hydriodic acid at  $125-130^{\circ}$ ; it crystallises from light petroleum in colourless prisms and melts at  $56-57^{\circ}$ .

$\delta$ -Chlorovaleric acid, produced by treating the preceding compound with freshly precipitated silver chloride, melts at  $18^{\circ}$  (compare Funk, Abstr., 1894, i, 34) and distils with partial decomposition at  $140-150^{\circ}$  under 15 mm. pressure, in this respect differing from its  $\alpha$ -,  $\beta$ -, and  $\gamma$ -isomerides.

$\delta$ -Valerolactone, formed on heating the  $\delta$ -chloro-acid at  $230-240^{\circ}$ , is prepared by boiling  $\delta$ -iodovaleric acid with alcoholic sodium ethoxide and distilling the product at  $215-220^{\circ}$ ; when pure, it boils at  $218-220^{\circ}$ .

$\delta$ -Bromovaleric acid results from the addition of hydrogen bromide to the preceding lactone, and is also prepared by heating  $\delta$ -phenoxyvaleric acid with concentrated hydrobromic acid, alkylating the crude product with ethyl alcohol saturated with hydrogen chloride, and hydrolysing the resulting ester with hydrobromic acid; it crystallises from light petroleum in monoclinic prisms and melts at  $39-40^{\circ}$ . The ethyl ester employed in this preparation boils between  $120^{\circ}$  and  $176^{\circ}$  under 15 mm. pressure.

G. T. M.

**Velocity of Esterification and the Electrical Conductivity of  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -Halogen Derivatives of Aliphatic Acids.** By DAVID M. LIGHTY (*Annalen*, 1902, 319, 369-390. Compare Abstr., 1896, ii, 557).—Experiments on the esterification of the  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -halogen derivatives of aliphatic acids show that the initial rate of esterification diminishes as the atomic weight of the halogen or the molecular weight of the acid increases; it also decreases when the substituent radicle passes from the  $\alpha$ - to the  $\beta$ -position. These differences, however, become less appreciable as the time of experiment is increased, and in those cases where there is no hydrolytic decomposition, the limits of esterification are practically the same. The limiting values, however, are usually vitiated by the hydrolytic changes which are indicated by the presence of chlorine, bromine, or iodine ions in the solutions under observation.

In the case of the  $\gamma$ -substituted acids, the hydrolytic decomposition

takes place so rapidly that measurements comparable with those recorded in the  $\alpha$ - and  $\beta$ -series cannot be obtained; this is also true, but to a less extent, in the case of the  $\delta$ -series.

The affinity constant (100  $K$ ), as measured by the electrical conductivity, decreases considerably as the halogen atom passes from the  $\alpha$ - to the  $\beta$ -position, the values for  $\alpha$ - and  $\beta$ -chloropropionic acids being 0.1465 and 0.0086 respectively.

In the  $\alpha$ -series, this constant diminishes as the molecular weight of the acid increases; the values obtained for chloroacetic,  $\alpha$ -chloropropionic, and  $\alpha$ -chlorobutyric acid are 0.155, 0.143, and 0.139 respectively. In the  $\beta$ -series, however, the constant for  $\beta$ -chloropropionic is smaller than that for  $\beta$ -chlorobutyric acid. Determinations of the electrical conductivity of the  $\gamma$ -substituted acids indicate that these compounds are very rapidly hydrolysed, the velocity of this change being greatest in the case of the bromo-compounds and least in that of the chloro-derivatives; the molecular conductivity decreases as the atomic weight of the halogen increases.

The affinity constant diminishes as the halogen atom passes from the  $\alpha$ - to the  $\delta$ -position, the values of the coefficients for  $\alpha$ -,  $\beta$ -, and  $\gamma$ -chlorobutyric and  $\delta$ -chlorovaleric acids being 0.1390, 0.0089, 0.0030 (?), and 0.0020 respectively.

The data employed in arriving at these conclusions are exhibited in tabular form, and the communication also contains several series of esterification and conductivity curves.

G. T. M.

**Action of Superheated Steam on Glycerol Esters of Fatty Acids.** By J. KLIMONT (*Zeit. angew. Chem.*, 1901, 14, 1269—1270).—In order to determine the relative ease with which various commonly occurring fats are hydrolysed by superheated steam, the fats were heated under various conditions of pressure and time in an autoclave, and the acid number of the fat determined. When heated with water under a pressure of 7 atmospheres for 8 hours, cocoa-nut fat and Japan wax were only very slightly hydrolysed, whilst other fats were considerably attacked; under 15 atmospheres pressure, this difference disappeared. On heating cocoa-nut fat, olive oil, or sesamé oil in a current of steam at 200° for half an hour, the cocoa-nut fat was scarcely affected, and the other two fats only slightly.

The results of the author's experiments are tabulated in the paper.

K. J. P. O.

**Synthesis of Derivatives of Ethyl Acetoacetate.** By MILORAD Z. JOVITSCHITSCH (*Ber.*, 1902, 35, 151—157).—Improved methods of preparing the following compounds are described: oxime of ethyl acetoacetate, nitrolic acid of ethyl acetate, ethyl chloroiminoacetate, ethyl phenylisonitrosoglycine, and ethyl phenylazodioxidiazinecarboxylate.

R. H. P.

**Action of Methyl Alcohol on Salts of Weak Acids.** By WILHELM WISLICENUS and WILLI STOEGER (*Ber.*, 1902, 35, 539—550. See *Abstr.*, 1899, i, 192).—The metallic derivatives of weak acids after prolonged boiling with methyl alcohol or sodium methoxide are often converted into basic methoxides, and these basic methoxides when suspended in boiling benzene are reconverted into the original compounds.

The following *basic methoxides* are described: that from the copper derivative of ethyl  $\alpha$ -chloroacetoacetate (small, slender, blue needles decomposing about  $180^\circ$ ), that from copper acetate ( $\text{COMe}\cdot\text{O}\cdot\text{Cu}\cdot\text{OMe}$ , microscopic, blue tablets), that from the magnesium derivative of ethyl acetoacetate. The *copper* derivative of methyl acetophenoneoxalate crystallises from methyl alcohol and melts at  $240\text{--}241^\circ$ . The copper derivative of benzoylacetone crystallises in small, bright green needles with MeOH. When an aqueous solution of nickel acetate is shaken with an ethereal solution of ethyl acetoacetate, the *compound*,  $\text{C}_{20}\text{H}_{32}\text{O}_{11}\text{Ni}_2$ , is obtained; this crystallises with EtOH in clusters of silky, greenish needles, and, when boiled with methyl alcohol, yields the *basic methoxide*,  $\text{C}_7\text{H}_{12}\text{O}_4\text{Ni}$ , which crystallises with MeOH and, when boiled with ethyl acetoacetate, yields the *nickel* derivative of ethyl acetoacetate which melts at  $228\text{--}230^\circ$ ; the analogous cobalt compounds are very similar; the *compound*  $\text{C}_{20}\text{H}_{32}\text{O}_{11}\text{Co}$  crystallises in compact, ruby-red prisms which decompose at about  $200^\circ$ , the *methoxide* crystallises with MeOH and decomposes at about  $135^\circ$ , and the *cobalt* derivative of ethyl acetoacetate crystallises in red, microscopic needles which melt at about  $207^\circ$ . The *nickel* derivative of ethyl oxalacetate crystallises in small, slender needles and melts at  $145^\circ$ . The *ferric* derivative of benzoylacetone crystallises from benzene and melts at  $224\text{--}225^\circ$ ; but neither this nor analogous ferric compounds yield basic methoxides.

R. H. P.

**Double Salts of Cadmium and Mercury.** By VOLKMAR KOHLSCHÜTTER (*Ber.*, 1902, 35, 483—492).—The first of a series of investigations of double salts containing different acid radicles undertaken to test the application of Werner's coordination theory to double salts.

Cadmium oxalate dissolves in a cold saturated solution of potassium chloride, and the solution, after standing for some hours, deposits quadratic crystals of the salt  $\text{Cd}_2[(\text{C}_2\text{O}_4)_3\text{Cl}_2]\text{K}_4, 6\text{H}_2\text{O}$ . The *bromide*,  $\text{Cd}_2[(\text{C}_2\text{O}_4)_3\text{Br}_2]\text{K}_4, 2\text{H}_2\text{O}$ , crystallises in round aggregates of tabular, prismatic crystals, and the analogous *nitrite*,  $\text{Cd}_2[(\text{C}_2\text{O}_4)_3(\text{NO}_2)_2]\text{K}_4, \text{H}_2\text{O}$ , in small, slender, quadratic plates. These compounds may be considered as bimolecular potassium cadmium oxalate,  $\text{Cd}_2(\text{C}_2\text{O}_4)_4\text{K}_4$ , in which one of the oxalic acid radicles has been replaced by  $\text{Cl}_2, \text{Br}_2$  or  $(\text{NO}_2)_2$ . When cadmium oxalate is dissolved in a solution of ammonium chloride, the salt  $\text{Cd}_4(\text{C}_2\text{O}_4)_3\text{Cl}_{10}(\text{NH}_4)_8$  is obtained in quadratic prisms.

The salt  $\text{Hg}_2[(\text{C}_2\text{O}_4)_3\text{Cl}_6]\text{K}_4$  was obtained by a similar method from mercuric oxalate in the form of cubical crystals.

The analogies existing between these compounds are discussed, as also is their constitution.

R. H. P.

**Synthesis of Organic Acids, Carbohydrates, and Albumin-like Substances.** By JULIUS WALTHER (*Chem. Zeit.*, 1901, 25, 1151).—By the electrolysis of aqueous solutions of carbon dioxide, the author states that he has obtained oxalic, citric, and tartaric acids, and also carbohydrates. In the presence of ammonia or ammonium salts, substances resembling albumin are formed.

K. J. P. O.

**Doubtful Points in the Application of Mendeléef's Periodic Law.** By N. TARUGI and Q. CHECCHI (*Gazzetta*, 1901, 31, ii, 417—445).—After discussing the positions of argon and of some of the rare earth

metals in the periodic classification of the elements, the author gives the following results of his measurements of the solubilities of the succinates, cinnamates, benzoates, and salicylates of magnesium, calcium, strontium, barium, and mercury; the numbers in the table below represent solubilities in percentages :

		At 15°.	At 100°.
Magnesium succinate	(+ 5H <sub>2</sub> O).....	24.3451	66.3593
Calcium	„ (+ 2H <sub>2</sub> O).....	1.2707	0.6615
Strontium	„ (monoclinic).....	0.4392	0.2145
Barium	„ .....	0.4009	0.2060
Mercury	„ C <sub>4</sub> H <sub>5</sub> O <sub>4</sub> Hg? (amorphous) ...	—	?
Magnesium benzoate	(+ 4H <sub>2</sub> O).....	5.8	16.4
Calcium	„ .....	8.6	10.2
Strontium	„ .....	5.2	5.6
Barium	„ (+ 6H <sub>2</sub> O).....	4.3	10.1
Mercury	„ (C <sub>6</sub> H <sub>5</sub> ·CO <sub>2</sub> ) <sub>2</sub> Hg? (amorphous)	1.2	2.5
Magnesium cinnamate	(+ H <sub>2</sub> O) ...	0.847	1.94
Calcium	„ (+ 3H <sub>2</sub> O) .....	0.21	1.15
Strontium	„ (+ 2H <sub>2</sub> O) .....	1.18	3.11
Barium	„ (+ 2H <sub>2</sub> O) .....	0.726	2.27
Mercury	„ (CHPh·CH·CO <sub>2</sub> ) <sub>2</sub> Hg? .....	—	0.527
Magnesium salicylate	(+ 4H <sub>2</sub> O) .....	20.40	79.68
Calcium	„ (+ 3H <sub>2</sub> O) .....	2.29	35.75
Strontium	„ (+ 2H <sub>2</sub> O) .....	3.04	20.44
Barium	„ (+ H <sub>2</sub> O) .....	26.85	54.08

It will be seen that, except in the case of the succinates, the different salts of any one of these acids exhibit properties which do not vary in any regular way with the atomic weights of the metals.

T. H. P.

**Synthesis of Dimethylsuccinic Acid under the Action of Light.** By W. SERNOFF (*Bull. Soc. Chim.*, 1902, [iii], 27, 14—16).—On shaking the ethyl ester of  $\alpha$ -iodopropionic acid in alcoholic solution with metallic mercury, while exposed to direct sunlight, mercuric iodide separates, and a mixture of the ethyl esters of the two dimethylsuccinic acids is produced.

A. F.

**Bromotrimethylsuccinic Acid and the  $\beta$ -Lactone of Trimethylmalic Acid.** By GUSTAV KOMPPA (*Ber.*, 1902, 35, 534—535. See *Abstr.*, 1899, i, 419, and compare Bone and Sprankling, *Trans.*, 1902, 81, 50).—A mixture of bromotrimethylsuccinic acid and its anhydride, when treated with moist silver oxide, yields the  $\beta$ -lactone of trimethylmalic acid,  $\text{CO} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{CMe}_2 \end{array} \text{CMe} \cdot \text{CO}_2\text{H}$ , which crystallises in flat needles, melts at 118—120°, and, when distilled, yields a crystalline compound melting at 66—67°, probably the anhydride of trimethylhydroxy-succinic acid.

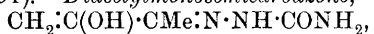
R. H. P.

**Physical Constants of  $\alpha$ -Ethylideneglutaric Acid.** By FRITZ FICHTER and BENNO MÜHLHAUSER (*Ber.*, 1902, 35, 341).—The

equivalent electrical conductivities of sodium  $\beta$ -ethylideneglutarate in solutions where  $v=32L$  and  $1024L$  differ by 11.9 units and not by 20 units as calculated from Ostwald's rule. This constant has also been determined for sodium  $\alpha$ -ethylideneglutarate and is found to be 16.4 or 15.5 when calculated in Siemens' reciprocal units. The dissociation constant  $K$  of  $\alpha$ -ethylideneglutaric acid is 0.0032, which agrees with the value 0.00281 observed for  $\beta$ -methyl- $\alpha$ -ethylideneglutaric acid.

G. T. M.

**Action of Semicarbazide on Diacetyl.** By OTTO DIELS (*Ber.*, 1902, 35, 347—351).—*Diacetylmonosemicarbazone*,



obtained by mixing together ice cold aqueous solutions of diacetyl and semicarbazide hydrochloride or the free base, separates from water in leaflets, and from glacial acetic acid in fusiform crystals; it melts and decomposes at 234—235° (corr.). The substance is a weak acid and dissolves in sodium hydroxide solution, the sodium salt separating out on concentration in yellowish-white needles. The salts are, however, dissociated by water and the semicarbazone itself is hydrolysed by warm mineral acids. When boiled with dilute acetic acid, the monosemicarbazone decomposes into diacetyl and diacetyl disemicarbazone.

*Diacetylmonoacetylhydrazone*,  $\text{CH}_3\text{C}(\text{OH})\cdot\text{CMe}\cdot\text{N}\cdot\text{NHAc}$ , is produced either by boiling diacetylmonosemicarbazone with acetic anhydride or by the interaction of diacetyl and acetylhydrazine in aqueous solutions; it crystallises from acetone in white needles melting at 166°. The hydrazone sublimes at temperatures below 100° and may be distilled without decomposition; it behaves as a weak acid, its concentrated sodium hydroxide solution yielding the sodium salt. The alkaline solutions of the hydrazone, when boiled, become turbid and deposit dimethylazethane. With dilute hydrochloric acid, the hydrazone yields its hydrochloride; the stronger acid, however, hydrolyses it into its generators.

G. T. M.

**Inversion of Sucrose.** By PAUL PETIT (*Compt. rend.*, 1902, 134, 111—112).—Direct determinations of the heat developed by the inversion of sucrose by dilute sulphuric acid give 2.639 Cal. at 58.5° and 2.675 Cal. at 63°, the probable value at 15° being 2.3 Cal. This value is lower than that obtained by Brown and Pickering (*Trans.*, 1897, 71, 783) for inversion by sucrase, but their determinations were made with comparatively small quantities of material.

C. H. B.

**Composition of Molasses from Pale Peat.** By HUGO BORNTRÄGER (*Zeit. anal. Chem.*, 1901, 40, 787—789).—The author communicates analyses by different chemists of three specimens of the saccharine substance obtained from peat by his process (D.R.-P. 122193; see also this vol., ii, 187). Although the results of the three analyses are somewhat differently expressed, they agree in showing 22 per cent. of reducing sugar (calculated as dextrose) in the dry substance.

M. J. S.

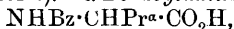
**Effect of Prolonged Boiling of Aqueous Solutions of Glycogen.** By JOSEPH NERKING (*Pflüger's Archiv*, 1901, **88**, 1—6. Compare Pflüger, *ibid.*, 1899, **75**, 120).—When aqueous solutions of glycogen are boiled for several days, the total amount of carbohydrates, when estimated by the cuprous oxide method after hydrolysis, remains the same, although appreciable amounts become transformed into carbohydrates soluble in alcohol. For example, after boiling for 12 days, 3.76, and for 14 days, 4.81 per cent. of the original carbohydrate becomes soluble. Similar effects are produced when glycogen is boiled with very dilute (0.1 per cent.) solutions of lactic acid, but are brought about much more readily. J. J. S.

**Preparation of Xylan.** By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1901, **34**, 162—180).—For the preparation of xylan, wheat straw is hydrolysed with 6 per cent. sodium hydroxide solution, filtered, and the xylan precipitated by the aid of Fehling's solution. The precipitate is triturated with dilute hydrochloric acid, then mixed with alcohol, washed with alcohol, and finally with ether. The yield is 22—23 per cent. of the straw. The composition agrees best with the formula  $C_{10}H_{18}O_9$ , whereas Tollens has previously ascribed the formula  $C_5H_8O_4$  to the compound. The specimen did not contain araban, mannan, or galactan, but small amounts of silica and cellulose were present as impurities. J. J. S.

**Aminovaleric Acids.** By MAX D. SLIMMER (*Ber.*, 1902, **35**, 400—410).— $\alpha$ -Aminoisovaleric acid (Clark and Fittig, *Annalen*, 1866, **139**, 200) was prepared by heating  $\alpha$ -bromoisovaleric acid with a saturated solution of ammonia and ammonium carbonate under pressure at  $100^\circ$ ; it melted and decomposed at  $298^\circ$  (corr.). The ethyl ester is an oil boiling at  $63.5^\circ$  under 8 mm. pressure, and at  $174^\circ$  with decomposition under atmospheric pressure, and having a sp. gr. 0.9617 at  $15^\circ/4^\circ$ ; the picrate of the ester forms small, yellow crystals melting at  $139.5^\circ$  (corr.); the hydrogen tartrate crystallises in prisms, and yields an amino-acid which is optically active. When kept, the ethyl ester changes to a solid, crystalline substance.  $\alpha$ -Benzoylaminoisovaleric acid,  $NHBz \cdot CHPr^{\beta} \cdot CO_2H$ , crystallises in leaflets melting at  $132.5^\circ$  (corr.).

With phenylcarbimide,  $\alpha$ -aminoisovaleric acid yields a substituted phenylcarbamide,  $NHPh \cdot CO \cdot NH \cdot CHPr^{\beta} \cdot CO_2H$ , which crystallises in colourless leaflets melting and decomposing at  $163.5^\circ$  (corr.), and is converted by boiling with hydrochloric acid into phenylisopropylhydantoin,  $CO \begin{matrix} \text{NH} \cdot CHPr^{\beta} \\ \diagup \quad \diagdown \\ \text{NPh} \cdot \text{CO} \end{matrix}$ ; this forms long needles melting at  $124—125^\circ$  (corr.).

$\alpha$ -Aminovaleric acid was prepared from  $\alpha$ -bromovaleric acid and melts and decomposes at  $291.5^\circ$  (corr.); the ethyl ester boils at  $68.5^\circ$  (corr.) under 8 mm. pressure and has a sp. gr. 0.9447 at  $15^\circ/4^\circ$ ; its picrate melts at  $115.6^\circ$  (corr.).  $\alpha$ -Benzoylaminovaleric acid,



prepared from the acid or the ethyl ester, melts at  $152.5^\circ$  (corr.). With phenylcarbimide,  $\alpha$ -aminovaleric acid gives a phenylcarbamide,  $NHPh \cdot CO \cdot NH \cdot CHPr^{\alpha} \cdot CO_2H$ , which crystallises in leaflets melting



and decomposing at  $119^{\circ}$  (corr.), and yields *phenylpropylhydantoin*,  $\text{CO} \begin{smallmatrix} \text{NH}-\text{CHPr}^a \\ | \\ \text{NPh}\cdot\text{CO} \end{smallmatrix}$ , melting at  $102^{\circ}$  (corr.).

*α-Amino-α-methylbutyric acid*,  $\text{NH}_2\cdot\text{CMeEt}\cdot\text{CO}_2\text{H}$ , was prepared by heating methyl ethyl ketone with anhydrous hydrogen cyanide under pressure at  $80^{\circ}$ ; the product is dissolved in alcoholic ammonia, and the solution, after a considerable interval, neutralised with hydrochloric acid; the acid crystallises in minute prisms melting at  $307.5^{\circ}$  (corr.); the copper salt crystallises, with  $3\text{H}_2\text{O}$ , in blue leaflets; the ethyl ester boils at  $65\text{--}66^{\circ}$  under 20 mm. pressure and yields a *picrate* which crystallises in leaflets melting at  $115\text{--}116^{\circ}$ . *α-Benzoylamino-α-methylbutyric acid*,  $\text{NHBz}\cdot\text{CMeEt}\cdot\text{CO}_2\text{H}$ , melts at  $198\text{--}199^{\circ}$  (corr.). The *phenylcarbamide* derivative,  $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CMeEt}\cdot\text{CO}_2\text{H}$ , forms crystals melting and decomposing at  $179\text{--}180^{\circ}$  (corr.), and yields *phenylmethylethylhydantoin*,  $\text{CO} \begin{smallmatrix} \text{NH}-\text{CMeEt} \\ | \\ \text{NPh}\cdot\text{CO} \end{smallmatrix}$ , crystallising in long needles melting at  $118^{\circ}$  (corr.).

*β-Aminoisovaleric acid* was prepared by heating dimethylacrylic acid with aqueous ammonia under pressure at  $150^{\circ}$ ; the ethyl ester boils at  $75^{\circ}$  under 22 mm. and at  $170^{\circ}$  under 760 mm. pressure and has a sp. gr. 0.8165 at  $20^{\circ}/4^{\circ}$ ; its *hydrochloride* is hygroscopic and melts at  $75^{\circ}$ . *β-Benzoylaminoisovaleric acid*,  $\text{NHBz}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , crystallises in leaflets melting at  $141.5^{\circ}$ . The compound with phenylcarbimide,  $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , crystallises in needles melting at  $137^{\circ}$  (corr.), and when boiled with hydrochloric acid, yields 1-phenyl-4-dimethylhydrouracil,  $\text{CO} \begin{smallmatrix} \text{NPh}-\text{CO} \\ | \\ \text{NH}\cdot\text{CMe}_2 \end{smallmatrix} \text{CH}_2$ , which crystallises in long, colourless needles melting and decomposing at  $237^{\circ}$ .

K. J. P. O.

**Synthesis of an Isomeride of Leucine.** By ALEXANDRE ÉTARD and A. VILA (*Compt. rend.*, 1902, 134, 122—124).—Active valeraldehyde,  $\text{CH}_2\text{Me}\cdot\text{CHMe}\cdot\text{CHO}$ , when treated with ammonia of sp. gr. 0.950, yields the calculated quantity of the ammonia compound,  $\text{C}_5\text{H}_{10}\text{O}\cdot\text{NH}_3\cdot 8\text{H}_2\text{O}$ , in white, optically active crystals, and this, when dried and treated with dry hydrogen cyanide, yields the calculated quantity of an oily cyanogen derivative,  $\text{C}_{12}\text{H}_{18}\text{N}_2$ , which boils at  $115\text{--}120^{\circ}$  under 30—40 mm. pressure, combines directly with a molecular proportion of bromine, and seems to have the constitution  $\text{C}:\text{N}:\text{N}:\text{C}$ .

$\begin{smallmatrix} \diagdown & \diagup \\ \text{CR}- & \text{CR} \\ \diagup & \diagdown \end{smallmatrix}$ . When hydrolysed with sulphuric acid, it yields a leucine, which crystallises very readily, has a persistent, sweet taste, and a solubility of 5.8 in 100 at  $18^{\circ}$ . It is not identical with the leucine of animal tissues, and contains two asymmetric carbon atoms.

C. H. B.

**Acetoacetamide.** By LUDWIG CLAISEN and K. MEYER (*Ber.*, 1902, 35, 583—584).—*Acetoacetamide*,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ , may be obtained by leaving ethyl acetoacetate in contact with 10 per cent. aqueous ammonia for several weeks, extracting the product with ether, and evaporat-

ing the aqueous solution under diminished pressure. It forms colourless crystals melting at  $50^{\circ}$ , and is readily soluble in water or alcohol, but insoluble in ether. Its copper derivative,  $(C_4H_6O_2N)_2Cu$ , forms green crystals. The *phenylhydrazone*,  $N_2HPh:CM_6:CH_2:CONH_2$ , melts at  $128^{\circ}$  and, in contact with mineral acids, yields 1-phenyl-3-methylpyrazolone. The *phenylazo*-derivative,  $N_2HPh:CAc:CONH_2$ , forms yellow crystals melting at  $151^{\circ}$ .

When heated, acetoacetamide is converted into the *amide* of Nieme and Pechmann's lutidonecarboxylic acid (Abstr., 1891, 675),  

$$NH_2 \cdot CO \begin{matrix} \swarrow CM_6:CH \\ \searrow CM_6:NH \end{matrix} > CO.$$

J. J. S.

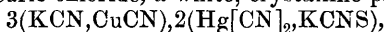
**Occurrence of Cyanogen Compounds in Coal-Gas, and of the Spectrum of Cyanogen in that of the Oxy-Coal-Gas Flame.** By WALTER NOEL HARTLEY (*Sci. Proc. Roy. Dublin Soc.*, 1901, 9, 289—297).—A reply to certain criticisms passed by Eder and Valenta on the author's previous work (*Phil. Trans.*, 1894, 185, 16). It is pointed out that Eder and Valenta, working on the same subject, burned the gas in a different manner; further, the Dublin gas supply has been shown to contain cyanogen compounds in sufficient quantity to account for the cyanogen spectrum obtained.

J. C. P.

**Quadrivalent Oxygen.** By KENDAL C. BROWNING (*Ber.*, 1902, 35, 93).—Attention is drawn to the fact that the compound of ferrocyanic acid and ether (*Trans.*, 1900, 77, 1233) is formed with development of heat from dry ferrocyanic acid and ether; it was previously regarded by the author as a compound in which oxygen was quadrivalent (compare Baeyer and Villiger, Abstr., 1901, i, 659).

K. J. P. O.

**Action of Potassium Cyanide on Cuprous Thiocyanate.** By HERRMANN ITZIG (*Ber.*, 1902, 35, 106—110).—Cuprous thiocyanate dissolves in a boiling 10 per cent. solution of potassium cyanide, and on cooling the solution a complex cyanide,  $KCN, Cu_2(CN)_2, H_2O$ , separates, identical with that obtained by Schiff and Becchi (*Annalen*, 1866, 138, 25). From the mother liquor crystallises, first, the salt,  $2KCN, Cu_2(CN)_2$ , described by Rammelsberg (*Ann. Phys. Chem.*, 1859, 106, 491), and finally a *thiocyanocyanide*,  $Cu_2(CN)_2, 4KCN, 2KCNS, H_2O$ , which forms microscopic needles very soluble in water. With aqueous copper sulphate, its solution gives at first a pale yellow precipitate which, on further addition of copper sulphate, becomes finally bluish-black; with mercuric chloride, a white, crystalline precipitate,



is produced which is fairly soluble in water.

Mercuric thiocyanate, when boiled with aqueous potassium cyanide, yields the complex salt  $Hg(CN)_2, KCNS$ , obtained by Boekmann (*Annalen*, 1837, 22, 239) and Cleve (*Bull. Soc. Chim.*, 1875, [ii], 23, 71).

K. J. P. O.

**Acetylenoid Metallic Radicles.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1902, [vii], 25, 65—67).—An account of work

already published, including a discussion of the results obtained by Chavastelon (Abstr., 1900, i, 324, 470; 1901, i, 494). G. T. M.

**Stereochemistry of Benzene.** By CARL GRAEBE (*Ber.*, 1902, 35, 526—531).—A discussion of various representations of the space formula of benzene. A new figure is favoured and is obtained by joining up by two edges three pairs of tetrahedra joined by two apices. This is practically a representation in space of the Kekulé formula and satisfactorily explains the following facts: that phthalic acid, but not isophthalic acid, forms an anhydride, that catechol alone of the dihydroxybenzenes forms a methylene ether and a carbonate, that two hydrogen atoms in benzene have never been replaced by one bivalent atom, that only one naphthalene or one fluorene, &c., is known, that such compounds as 1:8-naphthalene oxide are unknown. Like the Kekulé formula, however, it does not readily explain the identity of 1:2- and 1:6-disubstitution derivatives of benzene. R. H. P.

**Influence of different Atoms and Atomic Groups on the Conversion of Aromatic Sulphides into Sulphones.** By J. J. BLANKSMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 4, 264—266).—The steric influence of groups in the ortho-position in aromatic sulphides on the conversion of the latter into sulphones by means of nitric acid of sp. gr. 1.52 was investigated. Picryl sulphide, 3:5:3':5'-tetranitro-*o*-tolyl sulphide, and 2:2'-dicyano-4:6:4':6'-tetranitrophenyl sulphide, that is, symmetrically trisubstituted sulphides, are not oxidised by nitric acid, but 2:4:2':4'-tetranitrophenyl sulphide and *s*-trinitrothioanisole are readily converted into sulphones. The sulphone obtained from trinitrothioanisole melts at 218°. K. J. P. O.

**Triphenylmethyl. Correction.** By FRIEDRICH KEHRMANN (*Ber.*, 1902, 35, 622. Compare this vol., i, 89).—Gomberg was the first to suggest the quinonoid structure for so-called triphenylmethyl, and not Norris and Sanders as previously stated. J. J. S.

**Acetylation of Aromatic Amines.** By BRONISLAW PAWLEWSKI (*Ber.*, 1902, 35, 110—113, 622. Compare Abstr., 1898, i, 362).—Thioacetic acid is shown to be generally applicable for the acetylation of aromatic amines. *Diacetyldianisidide*, hitherto undescribed, crystallising in small leaflets melting at 242—243°, was prepared.

The method is especially applicable in the case of the aminobenzoic acids. K. J. P. O.

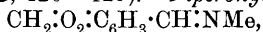
**Affinity Constants of certain Nitroamines and isoNitroamines.** By ARTHUR HANTZSCH [and, in part, M. BUCHNER] (*Ber.*, 1902, 35, 265—268. Compare *Baur*, Abstr., 1897, ii, 546).—Perfectly pure, colourless phenylnitromethane (Bamberger, Abstr., 1893, i, 326) is unimolecular in benzene solution and its affinity constant  $K=0.0023$  at 25°. The corresponding isonitroamine, nitrosophenylhydroxylamine, has the constant  $K=0.00046$ — $0.00057$  at 0°, and for nitrosobenzylhydroxylamine,  $C_6H_5 \cdot CH_2 \cdot N(NO) \cdot OH$ ,  $K=0.000583$  at 0° and  $0.000645$  at 25°.

The constant for phenylnitroamine rises rapidly with the temperature,

a characteristic feature of pseudo-acids which undergo ionising isomerism.

J. J. S.

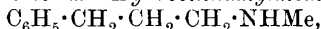
**Condensation of Aldehydes with Methylamine and Ethylamine and Reduction of the Condensation Products.** By CARL ANDREE (*Ber.*, 1902, **35**, 420—425).—*Piperonylenemethylamine*,



a white, waxy substance, melts at  $46^\circ$ , boils at  $148^\circ$  under 16 mm pressure, and is readily decomposed by dilute acids, *Piperonylmethylamine*,  $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3:\text{CH}_2\text{NHMe}$ , is a colourless oil, which boils at  $146^\circ$  under 12 mm. pressure, and is insoluble in water; the *hydrochloride* forms small, silvery flakes, dissolves readily in water, and melts at  $191^\circ$ ; the *hydrobromide* forms white scales, dissolves readily in water, and melts at  $191^\circ$ ; the *platinichloride* crystallises from alcohol in minute, yellow needles, and melts at  $182^\circ$  with frothing and decomposition; the *picrate* crystallises from alcohol in minute needles and melts at  $154^\circ$ .

*Piperonylene-ethylamine*,  $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3:\text{CH:NEt}$ , melts at  $51^\circ$  and is readily hydrolysed. *Piperonylethylamine*,  $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3:\text{CH}_2\text{NHEt}$ , is a colourless oil and boils at  $148^\circ$  under 20 mm. pressure; the *hydrochloride* forms thin, silky flakes, and decomposes and melts at  $201^\circ$ ; the *hydrobromide* forms silky flakes and melts at  $184$ — $185^\circ$ ; the *platinichloride* forms red needles and melts and decomposes at  $192^\circ$ ; the *picrate* crystallises from absolute alcohol in minute, yellow needles and melts at  $157^\circ$ ; the aurichloride could not be obtained owing to the separation of metallic gold.

*Cinnamylidenemethylamine*,  $\text{C}_6\text{H}_5:\text{CH:CH:CH:NMe}$ , is an oil which boils at  $134$ — $141^\circ$  under 16 mm. pressure, and was on one occasion obtained as a crystalline solid. *Hydrocinnamylmethylamine*,



is a colourless oil which boils at  $133$ — $135^\circ$  under 18 mm. pressure; the *hydrochloride* and *hydrobromide* were not analysed; the *platinichloride* forms yellow flakes and melts at  $181$ — $182^\circ$ ; the *aurichloride* is an oil; the *picrate* forms yellow needles and melts at  $93$ — $94^\circ$ .

*Cinnamylidene-ethylamine*,  $\text{C}_{11}\text{H}_{13}\text{N}$ , is a brown solid and boils at  $143$ — $145^\circ$  under 20 mm. pressure. *Hydrocinnamylethylamine*,  $\text{C}_{11}\text{H}_{17}\text{N}$ , is an oil which boils at  $124$ — $126^\circ$  under 25 mm. pressure; the *platinichloride* crystallises in yellow needles and melts at  $134$ — $135^\circ$ ; the *aurichloride* and *picrate* were obtained as oils.

*o-Nitrobenzylidenemethylamine*,  $\text{NO}_2:\text{C}_6\text{H}_4:\text{CH:NMe}$ , is an oil which boils at  $145^\circ$  under 23 mm. pressure. *o-Nitrobenzylidene-ethylamine* is an oil which decomposes when distilled even under reduced pressure.

T. M. L.

**Esters of Anilinomalonic Acid and their Derivatives.** By MAX CONRAD and H. REINBACH (*Ber.*, 1902, **35**, 511—525. Compare *Abstr.*, 1898, i, 589).—*Methyl anilinomalonate* separates from acetic acid in large, rhombic crystals, melts at  $68^\circ$ , and yields a *hydrochloride* which melts at  $133$ — $135^\circ$ , undergoing decomposition into carbon dioxide, methyl chloride, methyl alcohol, and diphenyldiketopiperazine; the *amide* crystallises in long, white prisms and melts at  $156^\circ$ . *Anilinomalonic acid* crystallises in colourless needles, melts and decomposes at

118—119°, and forms insoluble *calcium, silver, lead, zinc, and copper* salts, and an *aniline* salt, which crystallises in colourless, lustrous prisms melting and decomposing at 119°.

The remaining methylenic hydrogen atom in anilinomalonic acid is replaceable by sodium, giving compounds which react with alkyl haloids. *Methyl anilinomethylmalonate*,  $\text{NHPh} \cdot \text{CMe}(\text{CO}_2\text{Me})_2$ , crystallises from benzene or alcohol and melts at 97°, and the corresponding *amide* crystallises from water, softens at 183°, and melts at 187°. *Methyl anilino-benzylmalonate* crystallises in white prisms and melts at 94°. *Methyl o-nitrobenzylanilinomalonate* forms colourless prisms, melts at 157°, and, when reduced, yields *methyl 2-anilinohydrocarboxystyryl-2-carboxylate*,  $\text{C}_6\text{H}_4 \cdot \text{CH}_2 > \text{C} \begin{matrix} \text{NHPH} \\ \text{NH} - \text{CO} \end{matrix} \text{CO}_2\text{Me}$ , which melts at 171° and dissolves in hydrochloric acid, but is reprecipitated by water. *2-Anilinohydrocarboxystyryl* crystallises from acetic acid and melts at 178°. *Methyl anilinoethylene-tricarboxylate*,  $\text{NHPh} \cdot \text{C}(\text{CO}_2\text{Me})_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$ , crystallises from methyl alcohol and water and melts at 95°.

The anilinomalونات condense with the esters of unsaturated acids, forming substituted pyrrolidonedicarboxylates. *Ethyl 1:4-diphenylpyrrolidone-5:5-dicarboxylate* melts at 99°, the corresponding *methyl* ester crystallises in hard prisms melting at 130°, and the *acid* in prisms which melt and decompose at 178°. The monocarboxylic *acid*, obtained by heating the dibasic acid at 180°, melts at 147° and forms a *silver* salt which crystallises in small, slender needles.

The action of bromine on methyl anilinomalonate yields *methyl p-bromoanilinomalonate*, which crystallises in clusters of colourless needles melting at 84°. *Methyl dianilinomalonate* crystallises from methyl alcohol and melts at 124—125°.

The esters of anilinomalonic acid, when heated, condense with the formation either of indoxylates (see Blank, *loc. cit.*) or of derivatives of 2:5-diketopiperazine of the type of diindoxylic anhydride,  $\text{C}_6\text{H}_4 \cdot \text{N} - \text{CO} - \text{CH} \cdot \text{CO} \begin{matrix} | \\ \text{CO} - \text{CH} \cdot \text{CO} \cdot \text{N} - \text{C}_6\text{H}_4 \end{matrix}$ , which may be also prepared by prolonged heating of the indoxylates. *Diindoxylic anhydride* crystallises in lustrous, bright yellow leaflets and does not melt below 290°; and the *p-tolyl* (yellow, crystalline, insoluble powder) and the  *$\beta$ -naphthyl* derivatives are described.

Dibromobarbituric acid, when heated with aniline, is converted into the monobromo-acid. R. H. P.

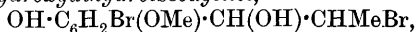
**Transformation of Imino-ethers into Acid Amides.** By WILHELM WISLICENUS and HEINRICH KÖRBER (*Ber.*, 1902, 35, 164—168).—A further discussion of results previously obtained (*Abstr.*, 1900, i, 435). The transformation of benzimino- $\beta$ -chloroethyl ether into  $\beta$ -chloroethylbenzamide, first observed by Gabriel and Neumann (*Abstr.*, 1892, 1331), is now shown to conform with the general rule for such transformations given by Wheeler and Johnson (*Abstr.*, 1900, i, 293). R. H. P.

**Tribromophenol Bromide.** By J. H. KASTLE [with A. S. LOEVENHART, ROSA SPEYER, and J. W. GILBERT] (*Amer. Chem. J.*, 1902, 27, 31—52).—*Tribromophenol bromide*, described by Benedikt (*Abstr.*,

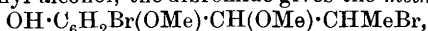
1879, 717), is obtained by the action of bromine on aqueous phenol in yellow crystals (m. p.  $118^{\circ}$ ). The molecular weight determined cryoscopically, using ethylene bromide as solvent, corresponds with that required for the formula  $C_6H_2OBr_4$ . By the action of heat, of light, or of iodine in carbon disulphide solution, it gives *hexabromophenoquinone*,  $C_{12}H_2OBr_6$ . This same substance has been obtained from tribromophenol and silver tribromophenoxide. When heated in a sealed tube at  $100^{\circ}$  with water, tribromophenol bromide gives a mixture of tribromophenol and tetrabromoquinone; with dry potassium iodide, it gives hexabromophenoquinone, but in aqueous solution potassium tribromophenoxide is produced. Its rate of decomposition is greatly accelerated by the presence of free bromine. Zinc ethyl gives with it zinc tribromophenoxide and ethyl bromide, and this is evidence that the constitution  $(C_6H_2Br_3 \cdot OBr)$  suggested by Benedikt is incorrect. To further prove the incorrectness of Benedikt's formula, it has been shown that tribromophenyl benzenesulphonate,  $C_6H_5 \cdot SO_2 \cdot OC_6H_2Br_3$  (m. p.  $99^{\circ}$ ), prepared by the action of sodium tribromophenoxide on benzenesulphonic chloride, cannot be obtained from tribromophenol bromide and sodium benzenesulphinat, but that the latter reaction again gives rise to hexabromophenoquinone. With silver nitrate solution, tribromophenol bromide gives *m*-dibromoquinone, and this reaction, as well as the others, can be explained by the formula suggested by Thiele and Eichwede (Abstr., 1900, i, 288). Tribromophenol bromide, when treated with sulphuric acid, suffers a molecular rearrangement and tetrabromophenol is formed. The analogous trichlorophenol bromide does not suffer a corresponding change. This rearrangement is explained on the basis of Thiele's theory of partial valency (Abstr., 1899, i, 554).

J. McC.

**Bromides of Eugenol and of *iso*Eugenol.** By KARL AUWERS and O. MÜLLER (*Ber.*, 1902, 35, 114—124).—Bromo*isoeugenol* dibromide,  $OH \cdot C_6H_2Br(OMe) \cdot CHBr \cdot CHMeBr$ , is not soluble in dilute alkalis, but behaves as a pseudo-phenol; with aqueous acetone, it yields *β*-*m*-dibromo-*α*-hydroxydihydroisoeugenol,



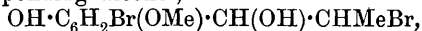
which crystallises from glacial acetic acid and melts at  $135$ — $136^{\circ}$ . With cold methyl alcohol, the dibromide gives the *methyl* ether,



which forms stout, colourless crystals and melts at  $104$ — $105^{\circ}$ ; the corresponding *ethyl* ether crystallises from alcohol and melts at  $78$ — $80^{\circ}$ . The *acetate*,  $OH \cdot C_6H_2Br(OMe) \cdot CH(OAc) \cdot CHMeBr$ , obtained by adding sodium acetate to a boiling solution of the dibromide in glacial acetic acid, is a bright yellow, transparent, waxy substance; its *benzoyl* derivative,  $C_{19}H_{18}O_5Br_2$ , crystallises from alcohol and melts at  $112$ — $114.5^{\circ}$ .

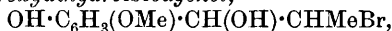
The foregoing methyl ether melting at  $104$ — $105^{\circ}$  is readily converted by boiling methyl alcoholic sodium methoxide into *bromo-α-β-dimethoxydihydroisoeugenol*,  $OH \cdot C_6H_2Br(OMe) \cdot CH(OMe) \cdot CHMe \cdot OMe$ , both bromine atoms of the dibromide being replaced by methoxyl groups; the product separates from alcohol in stout, colourless crystals, melts at  $81$ — $83^{\circ}$ , and yields a *benzoyl* derivative which forms colourless

crystals melting at 92—93°. *Bromo- $\alpha$ -hydroxy- $\beta$ -methoxydihydroisoeugenol*,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}(\text{OMe})\cdot\text{CH}(\text{OH})\cdot\text{CHMe}\cdot\text{OMe}$ , obtained similarly from the corresponding alcohol,



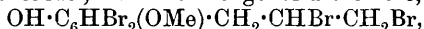
forms colourless crystals melting at 134—135°.

*$\beta$ -Bromo- $\alpha$ -hydroxydihydroisoeugenol*,



obtained from *isoeugenol* dibromide by the action of aqueous acetone, is a thick liquid which cannot be distilled or made to crystallise; its *methyl ether*,  $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}(\text{OMe})\cdot\text{CHMeBr}$ , is a syrup which yields a crystalline *benzoate* melting at 66—68°; the syrupy *ethyl ether* gives a *benzoate* melting at 72—73°, and is converted by bromine and hydrogen bromide in glacial acetic acid solution into *bromoisoeugenol* dibromide, a fact which indicates its structure.

The foregoing experiments show that whereas the  $\alpha$ -bromine atom of *isoeugenol* dibromides is easily replaced by hydroxy- and alkyloxy-groups, the  $\beta$ -bromine atom is only removed by alcoholic sodium methoxide or ethoxide; in *dibromoeugenol* dibromide,



the  $\beta$ - and  $\gamma$ -bromine atoms have a similar fixity, the substance not being acted on by boiling aqueous acetone or boiling alcohols.

The *acetyl* derivative of *bromoisoeugenol* dibromide forms colourless crystals and melts at 131—132°; that of *isoeugenol* dibromide crystallises in leaflets from alcohol and melts at 125—127°.

W. A. D.

**$\psi$ -Phenols from Salicylaldehyde and Salicylic Acid.** By KARL AUWERS and L. HUBER (*Ber.*, 1902, 35, 124—131. Compare Stoermer and Behn, *Abstr.*, 1901, i, 726; D.R.-P. 113723, 113512, 114194; and *Abstr.*, 1901, i, 727).—The iodide,  $\text{CHO}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}_2\text{I}$ , obtained from salicylaldehyde, formaldehyde, and hydriodic acid, crystallises from a mixture of benzene and light petroleum and melts at 125—126°, not at 87° as given in the German Patent. The *acetate*  $\text{CHO}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}_2\cdot\text{OAc}$ , is formed instantaneously when boiling acetic acid solutions of the corresponding iodide, chloride, or bromide and sodium acetate are mixed; it crystallises from glacial acetic acid in thick, colourless needles, melts at 61—62°, and does not behave as a  $\psi$ -phenol, inasmuch as it is soluble in dilute alkali and is not acted on by hot dilute acetone. The presence of methyl groups in the benzene nucleus thus appears to be necessary to confer  $\psi$ -phenolic properties on acetates of the type dealt with. The *oxime*,  $\text{C}_8\text{H}_9\text{NO}_3$ , of hydroxymethylsalicylaldehyde crystallises from a mixture of ethyl acetate and light petroleum in yellowish-white needles melting at 120—121°; the *oxime* of the foregoing acetate crystallises from benzene and light petroleum in needles melting at 133—134°. By boiling with acetic anhydride, both oximes are converted into the *diacetyl* derivative,  $\text{CN}\cdot\text{C}_6\text{H}_3(\text{OAc})\cdot\text{CH}_2\cdot\text{OAc}$ , of *hydroxymethylsalicylonitrile*, which separates from light petroleum in stout, white crystals and melts at 57—58°.

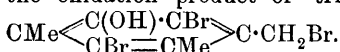
*$\alpha$ -3-Dibromomethylsalicylaldehyde* [ $\text{CHO}:\text{OH}:\text{Br}:\text{CH}_2\text{Br} = 1:2:3:5$ ],

obtained by adding bromine to a glacial acetic acid solution of the preceding acetate melting at  $62^\circ$  and subsequently passing hydrogen bromide into the hot liquid, crystallises from benzene in lustrous needles, melts at  $112\text{--}113^\circ$ , and is strongly  $\psi$ -phenolic; thus on warming with aqueous acetone it yields *3-bromo- $\alpha$ -hydroxymethylsalicylaldehyde*, which crystallises from benzene in yellowish-white needles and melts at  $84\text{--}85^\circ$ . The acetate,  $\text{CHO}\cdot\text{C}_6\text{H}_2\text{Br}(\text{OH})\cdot\text{CH}_2\cdot\text{OAc}$ , of this alcohol, obtained from the bromide by means of sodium acetate, is, however, a true phenol; it forms slender needles and melts at  $102^\circ$ .

$\alpha$ -Chloromethylsalicylic acid [ $\text{CO}_2\text{H}:\text{OH}:\text{CH}_2\text{Cl} = 1:2:5$ ] readily loses hydrogen chloride when left with methyl alcohol at the ordinary temperature, yielding the methyl ether,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}_2\cdot\text{OMe}$ , which melts at  $119^\circ$ , not at  $103^\circ$  as stated in the German Patent; on passing hydrogen chloride into the methyl alcoholic solution of the ether, the reverse change occurs, chloromethylsalicylic acid being formed.

*Methyl methoxymethylsalicylate*,  $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}_2\cdot\text{OMe}$ , is obtained by digesting the acid for several hours with methyl alcoholic hydrogen chloride (3—4 per cent.), and is a yellowish oil, soluble in alkalis; on passing hydrogen chloride through its methyl alcoholic solution at the ordinary temperature, it yields *methyl chloromethylsalicylate*,  $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}_2\text{Cl}$ , which crystallises from light petroleum in white needles and melts at  $65\text{--}66^\circ$  (compare German Patent). *Methoxymethylsalicylamide*,  $\text{NH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}_2\cdot\text{OMe}$ , crystallises from benzene in lustrous needles and melts at  $107\text{--}108^\circ$ . W. A. D.

**Constitution of the Second  $\psi$ -Cumenol Tribromide.** By KARL AUWERS and O. ANSELMINO (*Ber.*, 1902, 35, 131—144. Compare Abstr., 1900, i, 161—162).—The facts dealt with in this paper give confirmatory proof that the dibromohydroxy- $\psi$ -cumyl bromide melting at  $128^\circ$ , obtained by the action of hydrogen bromide on the diacetate of the oxidation product of tribromo- $\psi$ -cumenol, has the structure



*Dibromo-m-hydroxy- $\psi$ -cumylaniline*,  $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{NHPh}$ , obtained by digesting the bromide with aniline dissolved in benzene, crystallises from alcohol in small scales and melts at  $148\text{--}149^\circ$ ; the *diacetyl* derivative crystallises from methyl alcohol in aggregates of rhombic plates, melts at  $167\text{--}168^\circ$ , and on warming with dilute alcoholic sodium hydroxide yields the *monoacetyl* derivative,  $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{NAcPh}$ , which forms small, rhombic leaflets melting at  $216\text{--}218^\circ$ .

*m-Hydroxy- $\psi$ -cumylaniline*,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{CH}_2\cdot\text{NHPh}$ , obtained by reducing its dibromo-derivative with sodium amalgam, crystallises from a mixture of light petroleum and benzene in concentric aggregates of slender, silky needles melting at  $109\text{--}110^\circ$ ; the product was not quite pure, but contained 1.63 per cent. of bromine.

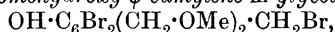
*o-Hydroxy- $\psi$ -cumylaniline* [ $\text{Me}_2:\text{OH}:\text{CH}_2\cdot\text{NHPh} = 1:2:4:5$ ], obtained by boiling *o*-hydroxy- $\psi$ -cumyl alcohol (Auwers and van de Rovaart, Abstr., 1899, i, 34) with aniline, crystallises from light



petroleum containing a few drops of benzene in soft, silky needles and melts at 139—140°; the *diacetyl* derivative crystallises from dilute alcohol in long, white needles melting at 68°, which are hydrated and lose their contained water when heated; the anhydrous substance melts at 85°. The *monoacetyl* derivative separates from light petroleum in nodules and melts at 137—138°.

*p*-Hydroxy- $\psi$ -cumylaniline  $[\text{Me}_2 : \text{OH} : \text{CH}_2 \cdot \text{NHPh} = 1 : 4 : 3 : 6]$  which is not produced when *p*-hydroxy- $\psi$ -cumyl alcohol is heated with aniline either alone or in presence of zinc chloride, is formed, however, in very small quantities when the components are heated in glacial acetic acid solution; it crystallises from alcohol in small prisms, softens at 201—202°, melts at 203—204°, and is also obtained, although in poor yield, by reducing the anil,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{Me}_2 \cdot \text{CH} : \text{NPh}$ , of 2 : 5-dimethyl-4-hydroxybenzaldehyde (Steckhan, *Diss.*, Heidelberg, 1900).

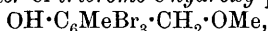
*s*-Pentabromo- $\psi$ -cumenol,  $\text{OH} \cdot \text{C}_6\text{Br}_2(\text{CH}_2\text{Br})_3$   $[\text{OH} : \text{Br}_2 = 1 : 2 : 5]$ , is obtained by heating dibromo- $\psi$ -cumenol with bromine for 8—10 hours at 130°, or pure dibromo-*m*-hydroxy- $\psi$ -cumyl bromide with bromine for 10 hours at 100°; it crystallises from glacial acetic acid in small, dull needles, melts at 174°, and is converted by boiling methyl alcohol into 3 : 6-dibromo-2 : 4-dimethoxydimethyl-5-bromomethyl-1-phenol (*dimethyl ether of tribromohydroxy- $\psi$ -cumylene-*m*-glycol*),



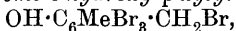
which separates from light petroleum in stellate aggregates of needles and melts at 113—114°. On reduction with zinc dust in glacial acetic acid, this yields 3 : 6-dibromo-2 : 4-dimethoxydimethyl-3-methyl-1-phenol, which crystallises from water in snow-white needles, melts at 94°, and is converted by hydrogen bromide in boiling glacial acetic acid solution into *dibromohydroxy- $\psi$ -cumylene dibromide*,

$\text{OH} \cdot \text{C}_6\text{Br}_2\text{Me}(\text{CH}_2\text{Br})_2$   $[\text{OH} : \text{Br}_2 : \text{Me} : (\text{CH}_2\text{Br})_2 = 1 : 2 : 5 : 3 : 4 : 6]$ ; the latter crystallises in rosettes of lustrous needles, and melts at 149—150°.

*s*-Pentabromo-*p*-xylenol (tribromohydroxy-*p*-xylylene dibromide, *m. p.* 184°; *Abstr.*, 1900, i, 160) is obtained by heating tribromo-*p*-xylenol with bromine for 5—6 hours at 130°, and is easily transformed by boiling methyl alcohol into the *methyl ether of tribromohydroxy-*p*-xylylene bromohydrin*,  $\text{OMe} \cdot \text{CH}_2 \cdot \text{C} \begin{smallmatrix} \text{CBr} & \text{CBr} \\ \diagdown & \diagup \\ & \text{C}(\text{OH}) : \text{CBr} \end{smallmatrix} \text{C} \cdot \text{CH}_2\text{Br}$ , which crystallises in compact crusts and melts at 125—126°. On reduction, it yields the *methyl ether of tribromo-*o*-hydroxy-*p*-xylyl alcohol*,



which crystallises from dilute methyl alcohol in small needles, melts at 62—63°, and on treatment with hydrogen bromide in hot glacial acetic acid solution gives *tribromo-*o*-hydroxy-*p*-xylyl bromide*,



crystallising from light petroleum in short, flat needles and melting at 117°.

W. A. D.

**Derivatives of Phenol Bromides.** By O. ANSELMINO (*Ber.*, 1902, 35, 144—150).—3 : 6-Dibromo-5-hydroxy- $\psi$ -cumyl bromide, when treated with pyridine, yields *dibromohydroxy- $\psi$ -cumylpyridine hydrobromide*, which crystallises in silky, hair-like needles melting at 237—238°.

When treated with potassium iodide, it gives *dibromohydroxy-ψ-cumyl iodide*, which crystallises in short compact needles, melts at 153—154°, and forms an *acetyl* derivative crystallising in needles and melting at 124—125°. The corresponding *chloride*, obtained by treating the diacetate of the alcohol (Abstr., 1900, i, 162) with hydrogen chloride, crystallises in white needles, melts at 99—100°, is easily soluble in most solvents, and forms an *acetyl* derivative which crystallises in needles melting at 94—95°.

2 : 4 : 6-*Tribromo-5-hydroxy-xylylene dibromide*, obtained by the action of bromine on the tribromohydroxy-xylene, crystallises from alcohol in small, felted needles, melts at 201°, is soluble in alkalis and not decomposed by boiling with acetone and water, being a normal phenol. On the other hand, dibromo-ψ-cumenol tribromide, when boiled with acetone and water, yields the *bromide* of *dibromohydroxy-ψ-cumylene-m-glycol*, which crystallises from ethyl acetate in compact prisms and melts and decomposes at 153°.

Tribromo-*p*-xylenol dibromide yields, when treated with aqueous acetone, the corresponding *bromhydrin* which crystallises in small needles melting at 142—143°; when treated with aniline, the *compound*,  $\text{CH}_2\text{Br} \cdot \text{C} \begin{smallmatrix} \text{CBr} & \text{CBr} \\ \text{CBr} & \text{C}(\text{OH}) \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{NHPh}$ , which crystallises in silky needles, and softens and decomposes without melting at 138—140°, and, when treated with *o*-toluidine, the corresponding *compound*, which is an orange-red, crystalline powder, and softens and decomposes at 120—125°.

The *ethyl* ether of dibromo-ψ-cumenol crystallises in fan-shaped clusters of needles melting at 55—56°; the *methyl* ether of tetrabromo-*o*-cresol in needles melting at 140·5°, and the *methyl* ether of tetrabromo-*m*-cresol in small needles melting at 145—146°, all three ethers being unattacked by moist bromine. R. H. P.

**Constitution of Oxidation Products from Halogenated ψ-Phenols.** By KARL AUWERS and A. SIGEL (*Ber.*, 1902, 35, 425—442).—Confirmation is given of Zincke's formula,



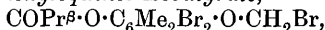
for the oxides obtained by the action of alcoholic potash on the halogenated ψ-quinols such as that,  $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CMe} \\ \text{CMe}:\text{CBr} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{OH} \\ \text{CH}_2\text{Br} \end{smallmatrix}$ , which is formed by oxidising tribromo-ψ-cumol. Addition of acetyl bromide or acetic anhydride to the oxides takes place, however, at the para-positions, giving compounds such as  $\text{OAc} \cdot \text{C} \begin{smallmatrix} \text{CBr}:\text{CMe} \\ \text{CMe}:\text{CBr} \end{smallmatrix} \text{C} \cdot \text{O} \cdot \text{CH}_2\text{Br}$

and  $\text{OAc} \cdot \text{C} \begin{smallmatrix} \text{CBr}:\text{CMe} \\ \text{CMe}:\text{CBr} \end{smallmatrix} \text{C} \cdot \text{OAc}$ , which have already been described, although formulated differently. Sulphuric acid causes this oxide, as well as the two additive products, to decompose into dibromo-*p*-xyloquinone,  $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CMe} \\ \text{CMe}:\text{CBr} \end{smallmatrix} \text{CO}$ , and formaldehyde.

*Dibromo-p-xyloquinol*,  $\text{OH} \cdot \text{C} \begin{smallmatrix} \text{CBr}:\text{CMe} \\ \text{CMe}:\text{CBr} \end{smallmatrix} \text{C} \cdot \text{OH}$ , forms white, glisten-

ing flakes, crystallises from acetic acid, and melts at 174—175°; the *diacetate* crystallises from acetic acid in small, white prisms and melts at 212—213°; the *monoacetyl* derivative is best prepared by hydrolysing acetylacetonaldibromo-*p*-xyloquinol, and its formation affords proof of the correctness of the formula now assigned to the latter; it forms stout, white or yellowish, glistening crystals, melts at 139—140°, crystallises from toluene, is slowly hydrolysed in alkaline solution to dibromoxyloquinol, and is converted by acetic anhydride into the diacetate; the *acetyl-benzoyl* derivative crystallises from methyl alcohol in white or yellowish prisms, melts at 162—163°, and is stable towards cold aqueous alkalis but quickly hydrolysed on heating.

*Bromomethyldibromoxyloquinol isobutyrate*,



from isobutyryl bromide and the oxide, crystallises from methyl alcohol in white, silky needles and melts at 88°. The *acetonyl isobutyrate*,  $\text{COPr}^\beta \cdot \text{O} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{O} \cdot \text{CH}_2\text{Ac}$ , prepared by the action of acetic acid and sodium acetate on the preceding compound, crystallises from light petroleum in white needles and melts at 55°; it is hydrolysed by methyl alcoholic sodium hydroxide to *dibromoxyloquinol monoisobutyrate*,  $\text{OH} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{O} \cdot \text{COPr}^\beta$ , which crystallises from light petroleum in minute, snow-white, glistening prisms, and melts at 119°; the *acetate*,  $\text{OAc} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CO}_2\text{Pr}^\beta$ , of the latter, which can also be prepared by the action of sodium isobutyrate on the acetyl bromide derivative of the original oxide, forms minute, white needles, and melts at 119°; its formation by these two methods affords evidence that the additive compounds of the oxide are derived from the quinol and not from the  $\psi$ -quinol.

The *methylene ether*,  $\text{CH}_2(\text{O} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{OAc})_2$ , of monoacetyldibromoxyloquinol, prepared by the action of methylene iodide on the sodium salt, forms white, thread-like needles, melts at 202°, and, like the methylene ether of tribromophenol, is only slowly hydrolysed by hot alkalis; it can also be prepared by the action on the sodium salt of the acetyl bromide derivative of the oxide, and therefore affords a direct proof of the constitution of the latter. T. M. L.

**$\psi$ -Quinols and Cyclic Nitroketones.** By KARL AUWERS (*Ber.*, 1902, 35, 443—455).—A theoretical paper containing a summary of the work of Zincke, Bamberger, and the author on the  $\psi$ -quinols. The last part of the paper deals with the similarly constituted nitroketones (compare the following abstract). T. M. L.

**Nitro-ketone and  $\psi$ -Quinol of Dibromo-*p*-cresol.** By KARL AUWERS (*Ber.*, 1902, 35, 455—464).—3:5-Dibromo-1-nitro-4-ketodihydrotoluene,  $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CH} \\ \text{CBr}:\text{CH} \end{smallmatrix} \text{CMe} \cdot \text{NO}_2$ , prepared by the action of nitric acid on dibromo-*p*-cresol, is a white, sandy compound, melts and decomposes at 62—65°, and rapidly becomes yellow and then brown on exposure to air and light. When left under water or aqueous alkalis or ammonium sulphide solution, or when moistened

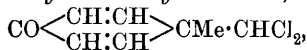
with alcohol and exposed to air, it is converted into 3-bromo-5-nitro-*p*-cresol,  $\text{OH} \cdot \text{C} \begin{smallmatrix} \text{CBr} \text{---} \text{CH} \\ \text{C}(\text{NO}_2) \text{:CH} \end{smallmatrix} \text{CMe}$ , which crystallises from light petroleum and melts at  $69^\circ$ ; its *acetyl* derivative crystallises from dilute acetic acid in glistening needles and melts at  $110\text{--}111^\circ$ .

3:5-Dibromo-1-methyl-4- $\psi$ -quinol,  $\text{CO} \begin{smallmatrix} \text{CBr} \text{:CH} \\ \text{CBr} \text{:CH} \end{smallmatrix} \text{CMe} \cdot \text{OH}$ , prepared by adding the nitro-ketone to acetic acid heated to  $40\text{--}50^\circ$ , or by leaving it exposed to the air in a desiccator, or by the action of nitrous fumes on a solution in acetic acid of dibromo-*p*-cresol, forms brilliant, diamond-like prisms and tablets belonging to the monoclinic system, crystallises from benzene, and melts at  $134.5^\circ$ . The isomeric quinol melts at  $149\text{--}150^\circ$  and not at  $117^\circ$  (Claus and Hirsch, Abstr., 1889, 389). Dibromo-*p*-hydroxybenzyl bromide,  $\text{OH} \cdot \text{C}_6\text{H}_4\text{Br}_2 \cdot \text{CH}_2\text{Br}$ , is formed as a bye-product in the preparation of the  $\psi$ -quinol from dibromo-*p*-cresol. The *acetyl* derivative of the  $\psi$ -quinol crystallises from dilute acetic acid in minute needles, from methyl alcohol in rhombic crystals, and melts at  $116\text{--}117^\circ$ . The *benzoyl* derivative crystallises from amyl alcohol in microscopic crystals, melts at  $204^\circ$ , and dissolves readily in alcohol and in acetic acid. The  $\psi$ -quinol and its esters are readily reduced to dibromo-*p*-cresol, whilst hydrogen bromide or phosphorus pentabromide gives tribromo-*p*-cresol. Tribromo-*p*-cresol melts at  $96^\circ$  (Wagner, *Diss. Marburg*, 1899, gives  $102^\circ$ ) and its acetate at  $72\text{--}73^\circ$  (Wagner gives  $77^\circ$ ); tetrabromo-*p*-cresol melts at  $193\text{--}194^\circ$  (Wagner gives  $196^\circ$ ) and yields a  $\psi$ -quinol, which is reduced again to the cresol by hydrogen bromide.

T. M. L.

**Cyclic Ketones from Chloroform and Phenols.** By KARL AUWERS and F. WINTERITZ (*Ber.*, 1902, 35, 465—471).—The chlorinated product formed on attempting to prepare hydroxydimethylbenzaldehyde by the action of chloroform and alkali on  $\psi$ -cumenol (Abstr., 1885, 380; 1886, 143) is shown to be a ketone constituted similarly to the  $\psi$ -quinols, and is now formulated as 1:2:4-trimethyl-2-dichloromethyl-5-ketodihydrobenzene,  $\text{CO} \begin{smallmatrix} \text{CMe} \text{:CH} \\ \text{CH} \text{:CMe} \end{smallmatrix} \text{CMe} \cdot \text{CHCl}_2$ ; it is reduced by zinc dust and acetic acid to methylene chloride and  $\psi$ -cumenol. The *dibromo*-derivative,  $\text{CO} \begin{smallmatrix} \text{CMe} \text{:CBr} \\ \text{CBr} \text{:CMe} \end{smallmatrix} \text{CMe} \cdot \text{CHCl}_2$ , prepared in a similar way from dibromo- $\psi$ -cumenol, crystallises from light petroleum in stout prisms and melts at  $99\text{--}100^\circ$ .

1-Methyl-1-dichloromethyl-4-ketodihydrobenzene,



from *p*-cresol and chloroform, crystallises from light petroleum in minute needles and melts at  $55^\circ$ . 1:3-Dimethyl-1-dichloromethyl-

4-ketodihydrobenzene,  $\text{CO} \begin{smallmatrix} \text{CMe} \text{:CH} \\ \text{CH} \text{=CH} \end{smallmatrix} \text{CMe} \cdot \text{CHCl}_2$ , from *as-m*-xylene, separates from light petroleum in stout crystals and melts at  $56^\circ$ .

*o*-Cresol and *p*-xylene, which do not contain a methyl group in the para-position to the hydroxyl, behave in the normal way and give only

the aldehyde; the aldehyde also appears as a bye-product in the case of *p*-cresol and *m*-xylenol. T. M. L.

**2:2'-Diphenol.** By OTTO DIELS and ARTHUR BIBERGEIL (*Ber.*, 1902, 35, 302—313).—2:2'-Diphenol sinters at 103°, melts at 109° (corr.), and boils at 325—326° (corr.) under 755 mm. pressure; when dissolved in hot water, it yields a crystalline, efflorescent *hydrate* melting at 71—73°. The dimethyl ether formed by its methylation is identical with that obtained by Jannasch and Költz (*Abstr.*, 1898, i, 190) from *o*-iodoanisole and sodium; the *ethylene ether*,  $\begin{matrix} \text{C}_6\text{H}_4\cdot\text{O} \\ \text{C}_6\text{H}_4\cdot\text{O} \end{matrix} > \text{C}_2\text{H}_4$ , obtained

by heating the diphenol with potassium hydroxide and ethylene bromide for 15 hours at 140—150°, crystallises from alcohol, on diluting with water, in lustrous, spindle-shaped needles and melts at 98° (corr.). The *urethane*,  $\text{C}_{12}\text{H}_8(\text{O}\cdot\text{CO}\cdot\text{NHPh})_2$ , obtained by heating the diphenol with phenylcarbimide for 15 hours at 100°, crystallises from dilute alcohol in beautiful needles and melts at 144—145° (corr.).

*Dibromo-2:2'-diphenol*, obtained by the action of bromine in chloroform solution at the ordinary temperature, melts at 188—189° (corr.); the *tetrabromo-derivative*, formed on brominating the diphenol in hot glacial acetic acid, crystallises from alcohol in silky needles with  $1\text{H}_2\text{O}$ , and melts at 204—205° (corr.). The action of chlorine on 2:2'-diphenol is so energetic that only the *tetrachloro-derivative* could be obtained; this crystallises from a mixture of benzene and light petroleum in needles and melts at 178° (corr.).

*3:3'-Dinitro-2:2'-diphenol*, obtained by nitrating the diphenol in glacial acetic acid solution at 0°, is purified by crystallising the product from absolute alcohol, when the isomeric dinitro-compound (*infra*) remains in solution; it crystallises in yellowish-brown needles, melts at 189—190° (corr.), and on reduction with tin and hydrochloric acid yields *3:3'-diamino-2:2'-diphenol*, which forms colourless needles, darkens at 190°, and melts and decomposes at 227° (corr.); the *dihydrochloride*, with  $2\text{H}_2\text{O}$ , forms colourless crystals.

*Tetra-acetyl-3:3'-diamino-2:2'-diphenol* crystallises from methyl alcohol, melts at 242° (corr.), and on distillation yields *bis-1-methylbenzoxazole*,  $\text{C}_{12}\text{H}_6\left(\begin{matrix} \text{N} \\ \diagup \text{O} \diagdown \end{matrix} > \text{CMe}\right)_2$ , which separates from alcohol in small plates, and melts at 150° (corr.); the formation of this shows the structure of the foregoing compounds.

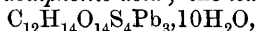
*5:5'-Dinitro-2:2'-diphenol* differs from its congener in being more soluble in boiling water and in alcohol; it crystallises in yellowish-brown needles, melts and decomposes at 240—250°, and on reduction yields *5:5'-diamino-2:2'-diphenol*, which forms slightly violet needles, melts at 246° (corr.), and cannot be recrystallised owing to its sparing solubility in all solvents; the *hydrochloride* forms greyish, cubical aggregates of needles, and is easily soluble in water.

*3:3':5:5'-Tetranitro-2:2'-diphenol*, obtained by nitrating the diphenol at 0° in glacial acetic acid and subsequently warming on the water-bath, crystallises best on slightly diluting its glacial acetic acid solution; it forms bright yellow crystals, melts at 248—249° (corr.), and on reduction yields a *tetra-amino-compound* which crystallises in small

needles and rapidly decomposes in the air; the *tetrahydrochloride*, forming small, grey or violet crystals, was analysed.

2 : 2'-*Dihydroxydiphenyl*-5 : 5'-*disulphonic acid* is formed on dissolving the diphenol in concentrated sulphuric acid at 50—60°; the *lead* salt, with 5H<sub>2</sub>O, forms large, lustrous crystals, and the *sodium* salt, which is very soluble in water, crystallises in plates. On nitration in aqueous solution, the free acid yields 5 : 5'-dinitro-2 : 2'-diphenol, a fact indicating its structure.

On sulphonation at 150°, the 2 : 2'-diphenol yields 2 : 2'-*dihydroxydiphenyl*-3 : 3' : 5 : 5'-*tetrasulphonic acid*; the *lead* salt,



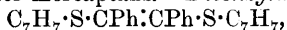
which is sparingly soluble in water, forms microscopic needles.

W. A. D.

**Extraction of Boletol.** By GABRIEL BERTRAND (*Compt. rend.*, 1902, 134, 124—126).—In order to extract boletol (this vol., ii, 166) from *Boletus*, the fungus must be freshly gathered, cut up into thin slices, and boiled for not less than half-an-hour with five times its weight of alcohol of 95°. The boletol is precipitated by means of lead acetate, liberated from the precipitate by the action of hydrochloric acid, and extracted with ether. Part of the boletol remains in the lead acetate precipitate, and if this is treated with ether, fats and boletol are dissolved together, and the boletol can be separated by treatment with water. The fats in the fungus have a marked power of dissolving boletol, and this fact can be utilised in isolating the substance. Boletol crystallises in slender needles, only slightly soluble in cold water, ether, or alcohol, but readily so in hot ether or alcohol, from which it does not separate on cooling.

C. H. B.

**Derivatives of Benzoin containing Sulphur.** By THEODOR POSNER (*Ber.*, 1902, 35, 506—510).—The substance obtained by the condensation of benzoin and ethyl hydrosulphide (Abstr., 1901, i, 15) is diethylthiolstilbene. Analogous compounds have been prepared by condensation with other mercaptans. *Dibenzylthiolstilbene*,



crystallises in needles melting at 174—175°, *diamylthiolstilbene* in long needles melting at 76—77°, and *diphenylthiolstilbene* in long needles, which sinter at 144° and melt at 160—162°.

R. H. P.

**Disulphones.** VIII. **Mercaptoles and Sulphones from Diketones.** By THEODOR POSNER (*Ber.*, 1902, 35, 493—505).—An elaboration of the fourth part (Abstr., 1901, i, 14). The action of phenyl, amyl, benzyl, and ethyl mercaptans on various diketones is compared. The methods employed are similar to those previously described (*loc. cit.*).

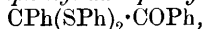
$\alpha$ -Diketones.— $\beta\beta\gamma\gamma$ -*Tetrabenzylthiolbutane* (*diacetyldibenzylmercaptole*),  $\text{CMe}(\text{S} \cdot \text{C}_7\text{H}_7)_2 \cdot \text{CMe}(\text{S} \cdot \text{C}_7\text{H}_7)_2$ , crystallises in short needles, melting at 164—165°\*, and when oxidised yields the corresponding *sulphone*, which crystallises in clusters of needles and melts at 195—196°.

$\beta\beta$ -*Diamylsulphonebutane- $\gamma$ -one* (*diacetyldiamylsulphone*) is a light yellow, clear oil. Phenyl hydrosulphide does not condense with

\* All melting points are corrected.

diacetyl or acetylpropionyl.  $\beta\beta$ -Dibenzylsulphonepentane- $\gamma$ -one is an uncrystallisable substance, which is precipitated when its alcoholic solution is cooled.  $\beta\beta$ -Diamylthiolpentane-3-one (acetylpropionylmonomylmercaptole) and the corresponding sulphone are oils.

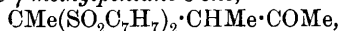
$\alpha\beta$ -Diphenyl- $\alpha\alpha$ -dibenzylthiolethane- $\beta$ -al (benzylmonobenzylmercaptole) crystallises in long, rhombic needles, melts at 101—103°, but does not yield a disulphone.  $\alpha\beta$ -Diphenyl- $\alpha\alpha$ -diphenylthiolethane-2-al,



crystallises in long needles, melts at 138°, and does not yield a disulphone.

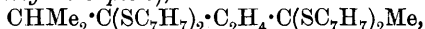
$\beta$ -Diketones.— $\beta\beta\delta\delta$ -Tetrabenzylthiolpentane (acetylacetonedibenzylmercaptole),  $\text{CMe}(\text{SC}_7\text{H}_7)_2 \cdot \text{CH}_2 \cdot \text{CMe}(\text{SC}_7\text{H}_7)_2$ , crystallises in clusters of long needles, melts at 65—66°, and, when oxidised, yields  $\beta\beta$ -dibenzylsulphonepentane- $\beta$ -one, which crystallises in white leaflets and melts at 137—138°.

$\beta\beta$ -Diamylsulphonepentane- $\delta$ -one is a light yellow, viscous oil.  $\beta\beta$ -Dibenzylsulphone- $\gamma$ -methylpentane- $\delta$ -one,



forms small, laminated crystals and melts at 149—151°.  $\beta\beta$ -Diamylsulphone- $\gamma$ -methylpentane- $\delta$ -one and  $\beta\beta$ -diphenylthiol- $\gamma$ -methylpentane- $\delta$ -one are oils, the latter yielding no sulphone.  $\alpha$ -Phenyl- $\gamma\gamma$ -dibenzylsulphone-butane- $\alpha$ -al (benzoylacetonedibenzylsulphone) melts at 70—76°;  $\alpha$ -phenyl- $\gamma\gamma$ -diamylthiolbutane- $\alpha$ -al and the corresponding sulphone are oils. The mercaptole, obtained by the condensation of benzoylacetone and phenyl hydrosulphide, does not yield a sulphone.

$\gamma$ -Diketones.— $\beta\beta\epsilon\epsilon$ -Tetrabenzylthiolehexane (acetonylacetonedibenzylmercaptole),  $\text{CMe}(\text{SC}_7\text{H}_7)_2 \cdot \text{C}_2\text{H}_4 \cdot \text{CMe}(\text{SC}_7\text{H}_7)_2$ , crystallises in long needles, melts at 98—99°, and when oxidised yields the corresponding sulphone, which sinters at 176° and melts and decomposes at 222—227°.  $\beta\beta\epsilon\epsilon$ -Tetraphenylthiolehexane is a colourless oil, but the corresponding sulphone crystallises in long needles melting at 139—140°.  $\beta\beta\epsilon\epsilon$ -Tetraphenylthiolehexane crystallises in small, lustrous needles, melts at 137—138°, and, in contradistinction to the mercaptols from  $\alpha$ - and  $\beta$ -diketones, yields a sulphone, which is a crystalline powder, melting and decomposing at 244°.  $\beta$ -Methyl- $\gamma\gamma\zeta\zeta$ -tetrabenzylthioleheptane (dimethylacetonylacetonebenzylmercaptole),



is a colourless oil, but the corresponding sulphone crystallises in laminæ and melts at 202—203°. The condensation product of dimethylacetonylacetone and phenyl hydrosulphide could not be purified, but when oxidised yielded  $\beta$ -methyl- $\zeta\zeta$ -diphenylsulphoneheptane- $\gamma$ -one, which is a crystalline powder melting at 117—118°.

R. H. P.

**The Comparison of Sulphoxides with Ketones.** By J. A. SMYTHE (*Proc. Univ. Durham*, 1901, 2, 9—10).—The analogy of benzyl sulphoxide to the ketones is chiefly structural, the sulphoxides being much more stable compounds than the ketones. Reduction of the sulphoxide does not lead to compounds analogous to the secondary alcohols or pinacones; alkaline reducing agents are without action on the sulphoxide, whilst acid reducing agents convert it into benzyl

sulphide. Phenylhydrazine and hydroxylamine are without action on the sulphoxide. The sulphoxide condenses with benzyl mercaptan, forming a crystalline compound melting at  $70^{\circ}$ . When acted on by phosphorus pentachloride, dibenzyl disulphide is formed. The author also shows that benzyl sulphide and hypochlorous acid yield benzylsulphonic chloride,  $C_6H_5 \cdot CH_2 \cdot SO_2Cl$ , melting at  $91-92^{\circ}$ . A. F.

Characterisation of "Pseudo-acids" by the Abnormal Relationship of their Affinity Constants and Hydrolysis of their Salts. By ARTHUR HANTZSCH and AD. BARTH (*Ber.*, 1902, **35**, 210—226. Compare Abstr., 1899, i, 399).—The usual relationship between the affinity constant of an acid and the hydrolysis of its sodium salt is represented by the formula  $x^2/(1-x)v = a^2/k$  where  $x$  is the percentage of sodium salt hydrolysed,  $v$  is the dilution in litres,  $a$  the dissociation factor of water, according to Van't Hoff, and  $k$  the affinity constant of the acid. This relationship has been shown by Walker (Abstr., 1900, ii, 268) to hold good for even very feeble acids.

The following conclusion has been previously drawn, namely, that when a non-conducting hydrogen compound yields an alkali salt which is not hydrolysed, or only very slightly so, then the alkali salt must have a different constitution from the original hydrogen compound, or abnormal neutralisation phenomena characterise a hydrogen compound as a pseudo-acid. As a rule, this phenomenon is rarely met with, as most pseudo-acids are electrolytes to a certain extent, and the alkali salts of these acids are hydrolysed to a certain extent.

The authors mention a second criterion by means of which pseudo-acids may be detected, namely, when the affinity constant and degree of hydrolysis do not agree with the above equation; in other words, when  $x^2/(1-x)v < a^2/k$ . The hydrolysis of the sodium salts may be determined by Shields' method (Abstr., 1893, ii, 448) or by Farmer's method (Trans., 1901, **79**, 863).

When the amount of hydrolysis is too small to estimate, the following argument is employed. A salt with a neutral or practically neutral action must correspond with a true acid, the ionisation of which must be at least as great as that of acetic acid ( $K = 180000 \times 10^{-10}$ ). If the affinity constant of the acid is much below that of acetic, then the hydrogen compound must be a pseudo-acid. As phenol ( $K = 1.3 \times 10^{-10}$ ) when strongly diluted has a distinctly acid action, all hydrogen compounds which are neutral are less strongly acid and must have a smaller constant; they must therefore, if they are true acids, yield sodium salts which are hydrolysed to a greater extent than sodium phenoxide (5.4 per cent. at  $v_{32}$  and  $25^{\circ}$ ). If the extent of hydrolysis is found to be much smaller, then the original hydrogen compounds must be pseudo-acids.

By this means, acetic, carbonic, boric, and hydrocyanic acids, hydrogen sulphide, and phenol have been proved to be true acids.

*iso*Nitrosophenylmethylpyrazolone, *isonitrosomethyl*pyrazolone, *isonitrosodiketo*hydrindene, *o*-toluquinoneoxime, *p*-quinoneoxime, *isonitroso*thiohydantoin, ethylnitrolic acid, isatinoxime, ethylisatinoxime, and *isonitroso*acetone have been characterised as pseudo-acids.

J. J. S.



### Characterisation of "Pseudo-acids" by the Ammonia Reaction.

By ARTHUR HANTZSCH and FRITZ E. DOLLFUS (*Ber.*, 1902, 35, 226—265. Compare *Abstr.*, 1899, i, 399).—The authors have employed the ammonia reaction previously described in order to determine whether various hydrogen compounds which give rise to salts are true acids or pseudo-acids. The method is readily applicable when the following conditions are fulfilled: (1) the compound yields an ammonium salt in ionising media, (2) the ammonium salt is insoluble in non ionising liquids, (3) the compound yields no precipitate of the ammonium salt with dry ammonia in the non-ionising liquids. As a rule, it is merely necessary to see whether the hydrogen compound yields a precipitate of the ammonium salt in ethereal, but not in benzene, light petroleum, or chloroform solution; if so, the compound must be a pseudo-acid provided the ammonium salt is insoluble in the media named.

A modified apparatus is described by means of which the amount of hydrogen compound transformed into ammonium salt may be estimated.

Under these conditions even the feeblest true acids, for example, phenols and oximes, combine with ammonia. The method possesses advantages over the electrochemical method, since it can be employed in non-ionising media, and thus the constitution of the undissociated hydrogen compounds determined. It is of special use in distinguishing between groups of isomeric and tautomeric substances and for detecting ionising isomerism. The conclusion that all compounds which combine directly with ammonia in benzene solution are true acids cannot be drawn, as a pseudo-acid may undergo isomerisation in the benzene solution under the influence of the ammonia. All enolic substances yield ammonium salts in non-ionising media, for example, the enolic forms of dibenzoylacetone, ethyl diacetylsuccinate, ethyl benzylideneacetoacetate, ethyl diketotetrahydropyridinecarboxylate, and oxymethylenecamphor. When both forms are sufficiently stable, the ammonia reaction serves as a simple method for the quantitative separation of the two isomeric (tautomeric) forms. The so-called ketopentamethylene derivatives consist almost entirely of the enolic forms, whereas ketohexamethylene compounds consist mainly of the ketonic forms; for example, ethyl diketohydrindenedicarboxylate is really ethyl hydroxyindonecarboxylate and ethyl phloroglucinoltricarboxylate, ethyl triketohexamethylenetricarboxylate. Ethyl acetoacetate and ethyl benzoylacetate react as ketones, ethyl oxalylacetate as an enol, and triphenylvinyl alcohol is probably triphenylethanone.

All acid amides are pseudo-acids; they possess in the solid and non-dissociated state the constitution  $R \cdot CO \cdot NHX$ , whereas their alkali salts have the constitution  $R \cdot C(OM) : NX$ . The true acids, the *iso*amides,  $R \cdot C(OH) : NX$ , have so far not been obtained in the solid state. The tendency of these pseudo-acids to pass over into salts or ions of the true acids increases with the negative nature of the X group (Br, Cl, CN,  $NO_2$ ).

Nitroamines,  $R \cdot NH \cdot NO_2$ , are also pseudo-acids and show a great tendency to undergo ionising isomerism. With camphenylnitroamine, the isomeric true acid,  $C_8H_{14} \begin{array}{c} \diagup CH \\ | \\ C : N : NO \cdot OH \end{array}$ , has been isolated and

melts at  $39^{\circ}$ ; the pseudo-acid,  $C_8H_{14} \begin{smallmatrix} CH_2 \\ | \\ C:N \cdot NO_2 \end{smallmatrix}$ , melts between  $65^{\circ}$  and  $70^{\circ}$  (Angeli, Abstr., 1897, i, 87).

Most  $\alpha$ -oximinoketones,  $R_1 \cdot CO \cdot C:(NOH)R_2$ , react as hydroxylic compounds, a few, for example, *syn*.benziloxime, isatoxime, and quinoxime, react as pseudo-acids.

Certain pseudo-acids (nitroamines) form additive products with ammonia, which become transformed into the true ammonium salts. These additive products probably correspond with the abnormal hydrates, which may be isolated from certain pseudo-acids.

The metallic derivatives of  $\beta$ -ketonic esters form unstable additive compounds with ammonia. J. J. S.

**Reduction of *m*-Aminobenzoic Acid.** By RUDOLPH BAUER and ALFRED EINHORN (*Annalen*, 1901, 319, 324—344. Compare Einhorn and Meyenberg, Abstr., 1894, i, 591).—*m*-Aminobenzoic acid when reduced with sodium and amyl alcohol gives rise to *m*-isoamylaminobenzoic acid, isoamylaminohexahydrobenzoic acid, aminohexahydrobenzoic acid, *m*-hydroxyisoamylbenzoic acid, *m*-hydroxyhexahydrobenzoic acid, and hexahydrobenzoic acid.

The *hydrochloride* of *m*-isoamylaminobenzoic acid separates, on acidifying the product of reaction with hydrochloric acid, in lustrous crystals and melts at  $257^{\circ}$ ; it dissolves but sparingly in alcohol, and is insoluble in ether or ethyl acetate. The acid  $C_5H_{11} \cdot NH \cdot C_6H_4 \cdot CO_2H$  is a solid substance, softening at  $47^{\circ}$  and melting at  $54^{\circ}$ . Its *nitroso*-derivative,  $NO \cdot N(C_5H_{11}) \cdot C_6H_4 \cdot CO_2H$ , crystallises from benzene in yellowish-white leaflets melting at  $131$ — $132^{\circ}$ , and giving the Liebermann reaction.

The other two amino-acids are isolated from the products of reduction in the form of their ethyl esters, the latter being prepared by boiling the crude hydrochlorides with alcohol saturated with hydrogen chloride. *Ethyl m-aminohexahydrobenzoate*,  $NH_2 \cdot C_6H_{10} \cdot CO_2Et$ , a colourless, pungent oil boiling at  $123^{\circ}$  under 11 mm. pressure, exhibits little tendency to form crystalline salts with acids; its *platinichloride*, an orange-coloured, granular, crystalline mass, decomposes at  $233^{\circ}$ . The *benzoyl* derivative and the *carbamide* are crystalline substances, melting at  $111^{\circ}$  and  $141^{\circ}$  respectively. The *chloroacetyl* derivative and *phenylthiocarbamide* crystallise in colourless needles, and melt respectively at  $115^{\circ}$  and  $149^{\circ}$ .

*m*-Aminohexahydrobenzoic acid,  $C_6H_{10} \begin{smallmatrix} NH_2 \\ | \\ CO \end{smallmatrix} O$ , resulting from the hydrolysis of the ethyl ester with boiling water, separates from this solvent on the addition of alcohol and acetone in colourless crystals melting at  $268$ — $269^{\circ}$ ; it sublimes in a vacuum and is neutral to litmus. The *hydrochloride*,  $CO_2H \cdot C_6H_{10} \cdot NH_2 \cdot HCl$ , crystallises from alcohol and ether in white leaflets and melts at  $156^{\circ}$ ; the *platinichloride* forms orange-coloured prisms decomposing at  $239^{\circ}$ . *m*-Hydroxyhexahydrobenzoic acid, produced by treating ethyl *m*-aminohexahydrobenzoate with nitrous acid and boiling the product with water, melts at  $125.5^{\circ}$ ; the melting point of this substance, as determined by Coblitz and Einhorn, being  $132^{\circ}$ .

*Ethyl m*-isoamylaminohexahydrobenzoate,  $C_5H_{11} \cdot NH \cdot C_6H_{10} \cdot CO_2Et$ ,

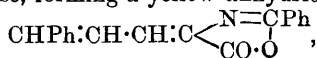
obtained from the reduction products of *m*-aminobenzoic acid or *m*-isoamylaminobenzoic acid in the manner indicated, is a colourless oil boiling at 153—155° under 11 mm. pressure; its *nitroso*-compound is a greenish-yellow oil, and its *aureichloride* forms yellow crystals melting at 131°.

The hydroxy-acids formed in the reduction of *m*-aminobenzoic acid are separated by fractional precipitation with hydrochloric acid from their solution in sodium carbonate. *m*-Hydroxy-*o*-isoamylbenzoic acid,  $C_5H_{11} \cdot C_6H_3(OH) \cdot CO_2H$ , the first fraction obtained in this manner, separates from benzene in colourless, lustrous crystals melting at 177°. *Ethyl m*-hydroxy-*o*-isoamylbenzoate,  $C_5H_{11} \cdot C_6H_3(OH) \cdot CO_2Et$ , produced by alkylating the acid with boiling alcohol saturated with hydrogen chloride, separates from light petroleum in silky, filiform crystals and melts at 75°; it dissolves in sodium hydroxide solution, and is reprecipitated by carbon dioxide.

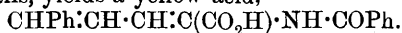
From the second fraction obtained by precipitation with hydrochloric acid, hexahydrobenzoic acid and *m*-hydroxyhexahydrobenzoic acid were isolated, the latter in the form of its *ethyl* salt; this ester boils at 140—150° under 11 mm. pressure, and yields a yellow *sodium* derivative. The reduction of *m*-aminobenzoic acid with sodium in ethyl alcohol leads to the formation of (1) aminohexahydrobenzoic acid, which is isolated in the form of its *ethyl* salt, boiling at 123° under 11 mm. pressure, and (2) *m*-hydroxy-*o*-ethylbenzoic acid,  $OH \cdot C_6H_3Et \cdot CO_2H$ , which crystallises from water in colourless, silky needles melting at 172°. The hydroxy-acid is readily soluble in the ordinary solvents; its *methyl* and *ethyl* esters are readily prepared from the corresponding alcohol and hydrogen chloride, the former crystallises in colourless leaflets melting at 71°, and the latter separates in filiform crystals which melt at 96°. The esters dissolve in solutions of sodium hydroxide, and are reprecipitated by carbon dioxide.

*m*-Acetoxy-*o*-ethylbenzoic acid,  $OAc_2 \cdot C_6H_3Et \cdot CO_2H$ , produced by adding concentrated sulphuric acid to an acetic anhydride solution of *m*-hydroxy-*o*-ethylbenzoic acid, crystallises from alcohol in colourless needles and melts at 145°. The corresponding *benzoyl* derivative, prepared by the Schotten-Baumann reaction, crystallises from dilute alcohol in colourless leaflets melting at 177°. These acyl derivatives are soluble in sodium carbonate solution. G. T. M.

**Synthesis of  $\alpha$ -Naphthoic Acid and Naphthalene.** By EMIL ERLÉNMEYER, jun., and J. KUNLIN (*Ber.*, 1902, 35, 384—386. Compare *Abstr.*, 1893, i, 580; 1899, i, 759).—Cinnamaldehyde and hippuric acid condense, forming a yellow anhydride,



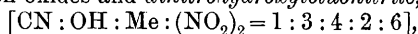
which, with alkalis, yields a yellow acid,



The latter is decomposed only slowly by alkalis, with the production of ammonia, phenylacetaldehyde, &c. When heated with excess of concentrated hydrochloric acid under pressure at 110—120° for 18 hours, a mixture of naphthalene,  $\alpha$ -naphthoic acid, and benzoic acid is formed. The yellow acid first decomposes into benzoic acid,

ammonia, and the  $\alpha$ -ketonic acid,  $\text{CHPh}:\text{CH}:\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , which then condenses with formation of the naphthalene ring. K. J. P. O.

**Tolyl Purpurates.** By WALTHER BORSCHKE and U. LOCATELLI (*Ber.*, 1902, 35, 569—576. Compare Abstr., 1900, i, 645).—It is probable that potassium purpurate is potassium nitrosonitrohydroxybenzonitrile,  $\text{NO}\cdot\text{C}_6\text{H}_3(\text{NO}_2)(\text{OK})\cdot\text{CN}$ . *Potassium o-tolylpurpurate*, [*potassium 1-methyl-4-cyano-3-nitroso-5-nitrophenoxide* (?)], obtained by the action of a warm concentrated solution of potassium cyanide on an alcoholic solution of dinitro-*o*-cresol, and purified by crystallisation from dilute potassium cyanide, is a dark-red, crystalline powder readily soluble in water but insoluble in alcohol or ether. Nitric acid decomposes it, yielding nitrogen oxides and *dinitrohydroxytoluonitrile*,



which crystallises in yellow, glistening needles melting at  $148\text{--}149^\circ$ ; it yields a *potassium* derivative crystallising in dark yellow needles which explode when heated.

The nitrile combines with aniline, yielding an *additive* product,  $\text{C}_8\text{H}_5\text{O}_5\text{N}_3\cdot\text{C}_6\text{H}_7\text{N}$ , which crystallises from water in yellow, glistening plates melting at  $156\text{--}158^\circ$ . On hydrolysis with potassium hydroxide, the nitrile yields the corresponding amide, *dinitrohydroxytoluamide*,  $\text{OH}\cdot\text{C}_6\text{HMe}(\text{NO}_2)_2\cdot\text{CONH}_2$ , in the form of glistening crystals melting at  $231^\circ$ , and also yielding a compound with aniline.

*Potassium p-tolylpurpurate* crystallises from 1 per cent. potassium cyanide in microscopic, brown needles, and on treatment with sodium nitrite and acetic acid yields an *acid*, the *silver* salt of which has the formula  $\text{C}_9\text{H}_5\text{O}_9\text{N}_5\text{Ag}_2$ . J. J. S.

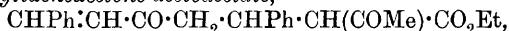
**Ketone and Acid Decomposition in the Ethyl Acetoacetate Series.** By EMIL KNOEVENAGEL [and, in part, A. FRIES] (*Ber.*, 1902, 35, 392—395).—Ethyl benzylidenebisacetoacetate, *p*-methylbenzylidenebisacetoacetate, and furfurylidenebisacetoacetate are decomposed by alkalis in the normal manner; with dilute alkalis, *cyclohexenones* are mainly formed, whilst with concentrated alkalis  $\beta$ -substituted glutaric acids are the chief products. Thus when ethyl benzylidenebisacetoacetate was boiled with a 10 per cent. potassium hydroxide solution, 73 per cent. of 3-phenyl-1-methyl-5-*cyclohexenone* and 17 per cent. of  $\beta$ -phenylglutaric acid were formed; with 60 per cent. potassium hydroxide, 4 per cent. of the ketone and 87 per cent. of the acid were obtained.

Ethyl *m*- and *p*-nitrobenzylidenebisacetoacetate, even with a 2 per cent. solution of potassium hydroxide, only yield the corresponding  $\beta$ -glutaric acids. On the other hand, ethyl citrylidene- and ethyl citronellidene-bisacetoacetates are not attacked by dilute alkalis, and with concentrated (80 per cent.) aqueous or alcoholic solutions only give ketones.

$\beta$ -Furfurylglutaric acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{C}_4\text{OH}_4)\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , forms crystals melting at  $134\text{--}135^\circ$ . K. J. P. O.

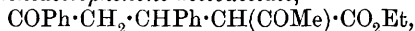
**Condensing Action of Organic Bases.** By EMIL KNOEVENAGEL and E. SPEYER (*Ber.*, 1902, 35, 395—399).—Ethyl acetoacetate and

dibenzylideneacetone condense in alcoholic solution at the ordinary temperature in the presence of a small quantity of diethylamine, forming *ethyl dibenzylideneacetone-acetoacetate*,



which crystallises in white needles melting at  $132^\circ$ . When treated with dry hydrogen chloride in chloroform solution or boiled with sodium hydroxide, *ethyl 3-cinnamenyl-5-phenyl- $\Delta^2$ -ketotetrahydrobenzene-6-carboxylate*,  $\text{CHPh} \cdot \text{CH} \cdot \text{C} \begin{smallmatrix} \text{CH}_2 \cdot \text{CHPh} \\ \text{CH} \text{---} \text{CO} \end{smallmatrix} \text{CH} \cdot \text{CO}_2\text{Et}$ , is produced; it crystallises in yellow plates melting at  $134^\circ$ .

*Ethyl benzylideneacetophenone-acetoacetate*,



prepared from benzylideneacetophenone and ethyl acetoacetate, crystallises in small, white needles melting at  $120\text{--}121^\circ$  and is converted by hydrogen chloride or sodium ethoxide into ethyl 3:5-diphenyl- $\Delta^2$ -ketotetrahydrobenzene-6-carboxylate (m. p.  $111\text{--}112^\circ$ , Abstr., 1895, i, 48). Benzylideneacetone and ethyl acetoacetate yield ethyl benzylidenebisacetoacetate (m. p.  $152^\circ$ , *loc. cit.*). K. J. P. O.

**Methyl Derivatives of Indigotin.** By MITSURU KUHARA and MASUMI CHIKASHIGÉ (*Amer. Chem. J.*, 1902, 27, 1—15. Compare Abstr., 1900, i, 560).—*Chloroacetylmethylanilide*,  $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{NMePh}$ , obtained by mixing chloroacetyl chloride with methylaniline, both in ethereal solution, crystallises from hot water in prisms and melts at  $61^\circ$ . When fused with potassium hydroxide, it is completely decomposed without giving any substance related to indigotin.

*Chloroacetyl-m-toluidide*,  $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$ , melting at  $141^\circ$ , was prepared from chloroacetyl chloride and *m*-toluidine. From the *o*- and *p*-compounds, diaryldiketopiperazines were prepared, and these, when fused with potassium hydroxide, gave dimethylindigotins.

5:5'-*Dimethylindigotin* can be obtained from chloroacetyl-*o*-toluidide or from di-*o*-tolylidiketopiperazine as a powder, which, when sublimed, crystallises in prisms closely resembling ordinary indigo in appearance. One gram of it is soluble in about 2000 c.c. of alcohol, or in 500 c.c. of chloroform; it is also soluble in ether, aniline, benzene, acetic acid, sulphuric acid, &c.

7:7'-*Dimethylindigotin* was similarly obtained from the corresponding para-compounds and 6:6'-*dimethylindigotin* from chloroacetyl-*m*-toluidide.

*Chloroacetyl-as-m-xylidide*,  $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$ , which melts at  $143^\circ$ , when treated with alcoholic potash, gives *di-as-m-xylidyldiketopiperazine*, which melts at  $170^\circ$ ; both of these, when fused with potassium hydroxide, give 5:7:5':7'-*tetramethylindigotin*.

4:5:7:4':5':7'-*Hexamethylindigotin* was similarly obtained from *chloroacetyl- $\psi$ -cumidide*, melting at  $158.5^\circ$ , which is prepared from chloroacetyl chloride and  $\psi$ -cumidine. The same indigotin derivative is obtained from di  $\psi$ -cumidyldiketopiperazine (m. p.  $221.5^\circ$ ).

The following positions of maximum darkness in the absorption bands of these various indigotins have been determined:

	$\lambda_1$	$\lambda_2$	$\frac{\lambda_1 + \lambda_2}{2}$
Indigotin .....	622.7	587.6	605.1
5:5'-Dimethylindigotin .....	643.6	615.7	629.7
6:6'-Dimethylindigotin .....	619.2	598.1	608.6
7:7'-Dimethylindigotin .....	642.7	622.7	633.2
5:7:5':7'-Tetramethylindigotin .....	662.7	631.7	647.2

The colours of solutions of these indigotins in various solvents are also given. J. McC.

**Derivatives of 3-Nitrophthalic Acid.** By ROBERT KAHN (*Ber.* 1902, 35, 471—472).—Contrary to the statement of Seidel (this vol., i, 159) both the possible nitroanthranilic acids (Hubner, Abstr., 1878, 148; 1880, 549) are formed by the action of hypobromite on 3-nitrophthalimide. T. M. L.

**Usnic Acid: Rotatory Power of other Lichen Derivatives.** By HEINRICH SALKOWSKI (*Annalen*, 1901, 319, 391—399. Compare Abstr., 1901, i, 152).—Hesse's contention that *Usnea longissima* contains *d*-usnic acid is confirmed. The *l*-acid from *Cladonia dactyloides*, *C. uncialis*, and *C. incrassata* has a mean  $[\alpha]_D - 489.2^\circ$ , whilst that from *Placodium crassum* has  $[\alpha]_D - 477.3^\circ$ . Leprarin, stictaurin, and placodiin have rotatory powers  $13.4^\circ$ ,  $-9.9^\circ$ , and  $-238.4^\circ$ . Glomellic acid and stereocaulic acid are inactive.

Usnic acid, obtained by Hesse by the fusion of usnic acid with potash (Abstr., 1901, i, 595), is identical with the author's usnetic acid. The latter designation has already been applied by Hesse to another product (Abstr., 1901, i, 645). The phenolic decomposition product, usnetol, obtained from the author's usnetic acid, is probably identical with the usnetol prepared by Paternò from pyroousnic acid. In preparing Paternò's pyroousnic acid, the readily oxidisable alkaline solution must be heated in an atmosphere of hydrogen, and not in oxygen as indicated in "Beilstein," II., 2058, 3rd edition. G. T. M.

**Compounds of Aromatic Aldehydes and the Esters of Aromatic Acids with Orthophosphoric Acid and its Alkyl Esters.** By P. N. RAIKOW and P. SCHATBANOW (*Chem. Zeit.*, 1901, 25, 1134—1138. Compare Abstr., 1900, i, 602, and 1901, i, 319).—In continuation of work previously published, the authors have prepared crystalline compounds of phosphoric acid with *p*-tolualdehyde and with vanillin, and also of phosphoric acid with methyl *p*-phthalate. The influence of the position and chemical nature of substituting groups on this capacity of forming compounds with phosphoric acid is discussed. K. J. P. O.

***cis*- and *trans*-Dibenzoylthylenes.** By CARL PAAL and HEINRICH SCHULZE (*Ber.*, 1902, 35, 168—176. See Abstr., 1901, i, 154).—*trans*-Dibenzoylethylene is quantitatively converted into the *cis*-form when

its solution in some organic solvent is exposed to daylight, the time required varying with different solvents up to 96 hours of daylight. When treated with hydrogen chloride, both isomerides yield *chloro-diphenacyl*,  $\text{COPh}\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{COPh}$ , which crystallises from ethyl acetate in six-sided, monoclinic tablets, melts and decomposes at  $141^\circ$ , and, when treated with sodium acetate, gives the *trans*-isomeride, thus affording a means of converting the *cis*- into the *trans*-form. The corresponding *bromo*-derivative forms similar crystals and melts and decomposes at  $139^\circ$ . Hydrogen iodide converts the *trans*-form into diphenacyl.

R. H. P.

**Phenanthraquinone Nitrate.** By FRIEDRICH KEHRMANN and M. MATTISSON (*Ber.*, 1902, **35**, 343—344).—*Phenanthraquinone nitrate*,  $\text{C}_{12}\text{H}_8\begin{matrix} \diagup \\ \text{C}:(\text{OH})\cdot\text{ONO}_2 \\ \diagdown \\ \text{C}:\text{O} \end{matrix}$ , obtained in lustrous, orange-red prisms by

dissolving the quinone in nitric acid of sp. gr. 1.4, is readily decomposed into its generators by water. Phenanthraquinone combines with sulphuric acid in a similar manner; its solution in the concentrated acid has a yellowish-green colour, and probably contains a disulphate; on diluting slightly, the colour changes to yellowish-red, and a sulphate corresponding with the nitrate separates in red needles. Chrysoquinone behaves in a similar manner towards sulphuric acid.

G. T. M.

**Sesquiterpene of Eucalyptus Oils.** By HENRY G. SMITH (*Chem. News*, 1902, **85**, 3).—Several eucalyptus oils contain in considerable quantity a sesquiterpene, *aromadendrene*, which boils at  $260$ — $265^\circ$ , has a sp. gr. 0.9249 at  $19^\circ$ , and when mixed with acetic acid and treated with bromine gives a crimson colour, changing through violet to deep indigo blue. It is this substance which gives the pink coloration when eucalyptus oils are tested for eucalyptol with phosphoric acid.

D. A. L.

**Oil of Jasmine Blossoms.** By ERNST ERDMANN (*Ber.*, 1902, **35**, 27—30).—This communication is mainly polemical (compare Hesse, *Abstr.*, 1900, i, 48, 454; 1901, i, 220, 732; and Erdmann, *Abstr.*, 1901, i, 601).

G. T. M.

**A New Constituent of German Oil of Sage.** By HEINRICH SEYLER (*Ber.*, 1902, **35**, 550—552. Compare Wallach, *Annalen*, **227**, 289; **252**, 104).—*Salvene*,  $\text{C}_{10}\text{H}_{18}$ , a liquid hydrocarbon, boiling at  $142$ — $145^\circ$ , has been obtained from German oil of sage. It has a sp. gr. 0.80 at  $20^\circ$ ,  $n_D$  1.4438, and a rotation of  $+1^\circ40'$ . When treated with 25 per cent. sulphuric acid, the boiling point of the hydrocarbon is raised some  $18$ — $20^\circ$ , and, when oxidised with permanganate, a ketonic acid is obtained the semicarbazone of which melts at  $204^\circ$ , whereas  $\beta$ -tanacetoketonic acid semicarbazone melts at  $202^\circ$ . The hydrocarbon *salvene* probably contains a bridged ring and has the formula  $\text{CH}_2\begin{matrix} \diagup \\ \text{CH} \\ \diagdown \end{matrix}\begin{matrix} \text{CHMe} \\ \diagup \\ \text{C}(\text{CHMe}_2)\cdot\text{CH}_2 \end{matrix}\diagdown \text{CH}_2$ .

J. J. S.

**Oxygen Bases.** By GEORG BREDIG (*Ber.*, 1902, 35, 271. Compare Walker, this vol., i, 170).—The author has already pointed out (*Zeit. Elektrochem.*, 1896, 3, 116) that ethylene oxide has only feebly basic properties. J. J. S.

**Dehydromucic Acid [Furfurandicarboxylic Acid].** By BERNHARD TOLLENS (*Ber.*, 1902, 35, 98).—A question of priority in the methods of formation of furfurandicarboxylic acid from mucic acid by means of acids (compare Yoder and Tollens, this vol., i, 49, and Hill, *Abstr.*, 1901, i, 555). K. J. P. O.

**Action of Methylamine and Ethylamine on Furfuraldehyde and Cuminaldehyde.** By G. SCHWABBAUER (*Ber.*, 1902, 35, 410—415. Compare Zaunschirm, *Abstr.*, 1888, i, 1077).—*Furfurylidenemethylamine*,  $C_4OH_3 \cdot CH:NMe$ , is formed when furfuraldehyde is mixed with aqueous methylamine, and is a colourless oil boiling at  $63^\circ$  under 14 mm. pressure. On reduction with sodium and alcohol, *methylfurfurylamine*,  $C_4OH_3 \cdot CH_2 \cdot NMe$ , is obtained as an oil boiling at  $65$ — $67^\circ$  under 21 mm. pressure; the *hydrochloride* of the base crystallises in white leaflets with a silky lustre melting at  $139^\circ$ ; the *hydrobromide* crystallises in small, white needles or leaflets melting at  $131^\circ$ ; the *picrate* in yellow needles melting at  $144^\circ$ . *Furfurylidene-ethylamine*,  $C_4OH_3 \cdot CH:NEt$ , is a colourless oil of disagreeable odour, boiling at  $60$ — $63^\circ$  under 14 mm. pressure; *furfurylethylamine*,  $C_4OH_3 \cdot CH_2 \cdot NEt$ , is an oil boiling at  $49$ — $50^\circ$  under 21 mm. pressure; the *hydrochloride* of the latter crystallises in white plates melting at  $120^\circ$ ; the *hydrobromide* in small, lustrous needles melting at  $113^\circ$ ; the *picrate* in yellow needles melting at  $111^\circ$ .

From cuminaldehyde and methylamine is obtained *cumylidene-methylamine*,  $C_6H_4Pr^{\beta} \cdot CH:NMe$ , which is an oil boiling at  $122^\circ$  under 14 mm. pressure. On reduction, *cumylmethylamine*,  
 $C_6H_4Pr^{\beta} \cdot CH_2 \cdot NMe$ ,

is produced as a colourless oil of pleasant odour boiling at  $121^\circ$  under 23 mm. pressure; its *hydrochloride* crystallises in white needles melting at  $165^\circ$ ; the *hydrobromide* in large, white plates melting at  $178^\circ$ ; the *platinichloride* in small, yellow needles melting at  $193^\circ$ ; the *aurichloride* in small, yellow needles melting at  $141^\circ$ , and the *picrate* in yellow needles melting at  $137^\circ$ .

*Cumylidene-ethylamine*,  $C_6H_4Pr^{\beta} \cdot CH:NEt$ , is a golden-yellow oil, boiling at  $149^\circ$  under 19 mm. pressure; the product of reduction, *cumylethylamine*,  $C_6H_4Pr^{\beta} \cdot CH_2 \cdot NEt$ , is an oily base of pleasant odour boiling at  $132^\circ$  under 19 mm. pressure; its *hydrochloride* crystallises in silver-white plates melting at  $180^\circ$ ; the *hydrobromide* in white plates melting at  $196^\circ$ ; the *aurichloride* in small, yellowish-green needles melting at  $131^\circ$ ; the *platinichloride* in reddish-yellow plates melting at  $179^\circ$ , and the *picrate* in yellow plates melting at  $122^\circ$ .

K. J. P. O.

**Basic Properties of Sulphur.** By ALBERT EDINGER and JOHN B. EKELEY (*Ber.*, 1902, 35, 96—98. Compare *Abstr.*, 1901, i, 166, 753).—The compounds obtained from aromatic bases and sulphur

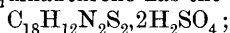


chloride are now believed by the authors to contain two quadrivalent basic sulphur atoms, and in consequence to have two additional hydrogen atoms respectively attached to the two sulphur atoms in the sulphur

ring,  $\begin{array}{c} \text{C} \cdot \text{SH} \cdot \text{C} \\ | \quad | \\ \text{C} \cdot \text{SH} \cdot \text{C} \end{array}$ . Analyses are given of the *tetranitrate* of thioquin-

anthrene,  $\text{C}_{18}\text{H}_{12}\text{N}_2\text{S}_2 \cdot 4\text{HNO}_3 \cdot 2\text{H}_2\text{O}$ , the *tetranitrate* of the base from sulphur chloride and *o*-toluquinoline,  $\text{C}_{18}\text{H}_{12}\text{N}_2\text{S}_2 \cdot 4\text{HNO}_3 \cdot 2\text{H}_2\text{O}$ , and the *tetranitrate* of *p*-toluthioquinanthrene,  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{S}_2 \cdot 4\text{HNO}_3$ . With acetyl chloride, the hydrochlorides of acetyl derivatives are obtained, in which the acetyl group is attached to sulphur. The *hydrochlorides* of acetylthioquinanthrene,  $\text{C}_{22}\text{H}_{16}\text{O}_2\text{N}_2\text{S}_2 \cdot 2\text{HCl}$ , of the acetyl derivative of the base from *o*-toluquinoline,  $\text{C}_{20}\text{H}_{16}\text{O}_2\text{N}_2\text{S}_2 \cdot 2\text{HCl}$ , and of acetyl-*p*-toluthioquinanthrene,  $\text{C}_{24}\text{H}_{20}\text{O}_2\text{N}_2\text{S}_2 \cdot 2\text{HCl}$ , have been analysed.

The *disulphate* of thioquinanthrene has the formula



that of *p*-toluthioquinanthrene,  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{S}_2 \cdot 2\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , is red, but when anhydrous, it forms a yellow solid.

K. J. P. O.

**Arginine and Ornithine.** By ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1901, **34**, 128—147. Compare Abstr., 1900, i, 110).—Ornithine chloride is optically active,  $[\alpha]_D +15.64$ — $16.8^\circ$ . The *platinichloride*,  $\text{C}_5\text{H}_{12}\text{O}_2\text{N}_2 \cdot \text{H}_2\text{PtCl}_6$ , forms a microcrystalline precipitate; the *picrate*,  $\text{C}_5\text{H}_{12}\text{O}_2\text{N}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , crystallises in stellate aggregates of prisms or in large, flat plates, and the *phosphotungstate* forms a precipitate soluble in boiling water. Ornithine, like lysine, is not precipitated on the addition of silver nitrate and baryta water. From E. Fischer's work (Abstr., 1901, i, 191) and also from that of Kutscher, it is probable that arginine is guanidine- $\alpha$ -aminovaleric acid.

Arginine is not decomposed when boiled for several hours with concentrated hydrochloric acid; at  $180$ — $200^\circ$  decomposition takes place and ammonium chloride is formed.

In the preparation of ornithine from arginine, the yield is not increased when other bases are substituted for baryta water. Sodium hypobromite readily decomposes arginine, and about one-third of the nitrogen is liberated.

J. J. S.

**Chelidoxanthin is Impure Berberine.** By JULIUS O. SCHLOTTERBECK (*Pharm. Review*, 1902, **20**, 4—5. Compare this vol., ii, 100).—By a study of its colour reactions, solubility in various solvents, &c., it is shown that Probst's chelidoxanthin is nothing more than impure berberine.

H. R. LE S.

**Creatine and Creatinine.** By ADOLF JOLLES (*Ber.*, 1902, **35**, 160—161).—Details of analyses which show that creatinine, like glycine (Abstr., 1901, i, 30), is comparatively stable towards permanganate in acid solution. This is explained by the assumption that both have a closed ring constitution of the nature of lactones.

R. H. P.

**Identification and Properties of  $\alpha$ - and  $\beta$ -Eucaïne.** By CHARLES L. PARSONS (*J. Amer. Chem. Soc.*, 1901, **23**, 885—893).— $\alpha$ -Eucaïne melts

at  $103^{\circ}$ ,  $\beta$ -eucaine at  $91^{\circ}$ , and their hydrochlorides melt and decompose at about  $200^{\circ}$  and  $268^{\circ}$  respectively. Both these bases, like cocaine, are precipitated by ammonia, but  $\alpha$ -eucaine is distinguished from the others by being almost insoluble in excess of the reagent. Potassium iodide gives a white, glistening precipitate with solutions of  $\alpha$ -eucaine hydrochloride, but does not yield a precipitate with  $\beta$ -eucaine or cocaine. When potassium dichromate is added to a solution of  $\alpha$ -eucaine, an almost insoluble, lemon-yellow precipitate is produced, which is increased on addition of hydrochloric acid;  $\beta$ -eucaine and cocaine are not precipitated by potassium dichromate until after the addition of hydrochloric acid, when a yellow precipitate appears which readily dissolves in excess of hydrochloric acid or on dilution with water.

If cocaine hydrochloride is triturated with dry mercurous chloride and then moistened with alcohol, it rapidly becomes greyish-black;  $\alpha$ -eucaine slowly turns dark grey under these conditions, whilst  $\beta$ -eucaine is not affected. On addition of platonic chloride to a 1 per cent. solution of cocaine hydrochloride, a yellow, crystalline precipitate is produced, which is insoluble in hydrochloric acid, whilst solutions of  $\alpha$ - and  $\beta$ -eucaine hydrochloride of the same strength do not yield a precipitate. When a small quantity of a solution of the hydrochloride is treated with a drop of potassium permanganate solution, in the case of the eucaines the solution rapidly turns brown, whilst with cocaine the colour is not completely changed in half-an-hour.

$\beta$ -Eucaine hydrochloride is distinguished from cocaine hydrochloride by its comparative insolubility in water or alcohol.

The microscopic characters of the hydrochlorides of the three alkaloids under polarised light are described. E. G.

**Pilocarpine.** By ADOLF PINNER and R. SCHWARTZ (*Ber.*, 1902, 35, 192–210. Compare Pinner and Kohlhammer, *Abstr.*, 1900, i, 456, 685; 1901, i, 340; Jowett, *Trans.*, 1901, 79, 1331).—The experiments made by Pinner and Kohlhammer have been repeated and the results confirmed with the exception that piluvic acid, or *homopilomalic acid* as the authors prefer to call it, is probably  $C_8H_{14}O_5$  and not  $C_8H_{12}O_5$ .

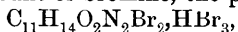
The amide of piluvic acid melts at  $206^{\circ}$ ; Jowett gives  $208^{\circ}$ .

When pilocarpine or *isopilocarpine* is oxidised at the ordinary temperature with potassium permanganate (3 mols.), the chief product is the acid  $C_8H_{14}O_5$ ; when chromic acid is employed, an acid,  $C_{11}H_{16}O_5N_2$ , is obtained which, on oxidation with permanganate at the ordinary temperature, yields an acid,  $C_7H_{12}O_5$ , previously described as *isohydrochelidonic acid*, but now called *pilomalic acid*.

The acid,  $C_7H_{12}O_5$ , when heated at its melting point, loses a mol. of water yielding a non-crystallisable dibasic acid,  $C_7H_{10}O_4$ , isomeric with Jowett's pilopic acid; this gives a *barium* salt,  $C_7H_{10}O_4Ba$  or  $C_7H_8O_4Ba$ . Pilomalic acid is lævorotatory and has  $[\alpha]_D -11.7^{\circ}$ .

A solution of *isopilocarpic acid* may be obtained by passing carbon dioxide into an absolute alcoholic solution of its salt and filtering off the alkali carbonate. When the solution is warmed, *isopilocarpine* is formed, but when concentrated under reduced pressure, a substance,  $C_{11}H_{18}O_3N_2 \cdot H_2O$ , is obtained.

*iso*Pilocarpic acid *platinichloride* forms nodular crystals melting at 180°. Pilocarpic acid cannot be isolated from its salts in a similar manner and also differs from *iso*-acid in that its hydrochloride yields no precipitate with mercuric chloride. Both acids in the free state combine with mercuric chloride, yielding compounds of the formula  $C_{11}H_{16}O_2N_2.HgCl_2$ ; the one from pilocarpic acid softens at 127° and melts at 145°, that from *iso*-acid melts at 164°. No definite additive compound of pilocarpine and bromine has been prepared. Even when only 2 atoms of bromine in chloroform solution are employed for 1 molecule of the base, the resulting product is dibromopilocarpine, whilst with a larger amount of bromine, the perbromide,



is formed. Dibromopilocarpine,  $C_{11}H_{14}O_2N_2Br_2$ , melts at 94° and not at 79° as previously stated. Bromocarpic acid has been obtained in a crystalline state (compare Jowett, *loc. cit.*); it melts at 209° and not at 194° and has  $[\alpha]_D - 90.5^\circ$ .

The indifferent substance previously obtained by the oxidation of pilocarpine with permanganate is probably methylcarbamide.

Pilocarpine crystallises in long needles melting at 34°. J. J. S.

**Yohimbine.** By CARL ARNOLD and M. BEHRENS (*Chem. Zeit.*, 1901, 25, 1083).—Yohimbine hydrochloride,  $C_{22}H_{28}O_3N_2.HCl$ , obtained from the bark of the Yohimbehe, a tree of the Cameroons, closely resembles cocaine hydrochloride in physiological action. The authors have made a careful comparison of the chemical and physical characters of the two salts.

K. J. P. O.

**Formation of the Pyrrolidine Ring.** By RICHARD WILLSTÄTTER and FRIEDRICH ETTLINGER (*Ber.*, 1902, 35, 620—622. Compare Abstr., 1900, i, 405).—Ethyl dibromopropylmalonate and methylamine yield the methylamide  $CH_2 \begin{smallmatrix} \text{NMe} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{C}(\text{NHMe}) \cdot \text{CO} \cdot \text{NHMe}$ , which, on hydrolysis with barium hydroxide, yields one mol. of methylamine and the methylamide  $CH_2 \begin{smallmatrix} \text{NMe} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{NHMe}$  whereas on hydrolysis with hydrochloric acid at 120—130° it yields 1-methylpyrrolidine-2-carboxylic acid, in the form of its hydrochloride.

J. J. S.

**Cyclic Quaternary Ammonium Salts.** By EDGAR WEDEKIND (*Ber.*, 1902, 35, 178—185. Compare Menshutkin, Abstr., 1895, ii, 385; Evans, Trans., 1897, 71, 552).—1-Benzylpiperidinium iodide *ethyl acetate*, obtained by the combination of benzylpiperidine and ethyl iodoacetate or of ethylpiperidinoacetate and benzyl iodide, crystallises from a mixture of chloroform and benzene or chloroform and acetone in monoclinic, prismatic needles melting at 193—194° [ $a:b:c = 1.6160:1:0.8215$ ;  $\beta = 84^\circ 11'$ ]. It dissolves readily in warm alcohol or water. The corresponding bromide, formed by the combination of benzylpiperidine and ethyl bromoacetate or of ethyl piperidinoacetate and benzyl bromide (Abstr., 1901, i, 639), melts at 192°.

*Methyl piperidine-1-acetate*,  $C_8H_{15}O_2N$ , obtained by the action of

methyl chloroacetate on piperidine, is a colourless oil distilling at 205—207°, which combines with benzyl bromide to form a *quaternary* salt melting at 193—194°, identical with the product obtained from benzylpiperidine and methyl bromoacetate.

*Benzylallylpiperidinium bromide*,  $C_3H_5 \cdot C_5NH_{10}Br \cdot C_7H_7$ , obtained from 1-benzylpiperidine and allyl bromide, forms colourless prisms decomposing at 161°.

1-*Allyltetrahydroquinoline* may be obtained by the action of allyl bromide or iodide on tetrahydroquinoline, or by the reduction of quinoline allyl iodide with tin and hydrochloric acid; it is a pale yellow liquid boiling at 264—266° under 755 mm. pressure; the *hydrobromide* crystallises from alcohol and melts at 164—165°.

*Methylallyltetrahydroquinolinium iodide*, obtained by the combination of kairiline with allyl iodide or of 1-allyltetrahydroquinoline with methyl iodide, crystallises in yellowish, monoclinic prisms [ $a:b:c = 0.6677:1:0.4957$ ;  $\beta = 70^\circ 28.5'$ ]. It decomposes at 143° and is readily soluble in warm water, alcohol, or chloroform.

1-*Benzyltetrahydroquinoline* distils at 218—222° under 38 mm. pressure, crystallises from alcohol in colourless needles melting at 36—37°, and combines only slowly with ethyl iodide. J. J. S.

**Condensation of 6-Phenyl-2-methylpyridine with Aldehydes.** By E. THORAUSCH (*Ber.*, 1902, 35, 415—419. Compare Dehnel, *Abstr.*, 1901,i,165).—6-*Phenyl-2-o-nitrostilbazole*,  $C_6NH_3Ph \cdot CH:CH \cdot C_6H_4 \cdot NO_2$ , prepared by condensing 6-phenyl-2-methylpyridine with *o*-nitrobenzaldehyde, crystallises from dilute alcohol in yellow needles and melts at 62°; the *hydrochloride* forms lemon-yellow, hair-like crystals and melts at 186—187°; the *hydrobromide* forms yellow needles and melts at 238°; the *aurichloride*,  $(C_{19}H_{14}O_2N_2, HCl)_2AuCl_3 \cdot 2H_2O$ , forms yellow needles and melts at 126°; the *platinichloride* forms short, orange-red needles and melts at 200°; the *mercurichloride* crystallises from dilute alcohol in white needles and melts at 219°.

The *dibromide*,  $C_6NH_3Ph \cdot CHBr \cdot CHBr \cdot C_6H_4 \cdot NO_2$ , crystallises from dilute alcohol in white needles and melts at 145°.

6-*Phenyl-2-m-nitrostilbazole*, prepared in a similar manner to the *o*-compound, forms yellow needles and melts at 139°; the *hydrochloride* forms long, slender, yellow needles and melts at 216°; the *hydrobromide* crystallises from dilute alcohol in small, pale yellow needles and melts at 263°; the *aurichloride*,  $C_{19}H_{14}O_2N_2, HCl, AuCl_3$ , forms yellow needles, dissolves readily in hot alcohol, and melts at 178—179°; the *platinichloride* forms small, orange-coloured needles, does not dissolve readily in alcohol, and melts at 262°.

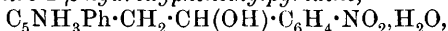
The *dibromide*,  $C_{19}H_{14}O_2N_2Br_2$ , crystallises from hot alcohol in white needles, and melts at 189°.

6-*Phenyl-2-piperonylalkidine*,  $C_5NH_3Ph \cdot CH:CH \cdot C_6H_3 \langle \bigcirc \rangle CH_2$ , prepared by condensing phenylmethylpyridine with piperonaldehyde, crystallises from dilute alcohol in white needles and melts at 155°; the *hydrochloride* crystallises from dilute alcohol in yellow needles and melts at 239°; the *aurichloride* forms golden-yellow needles,

but decomposes on recrystallising; the *platinichloride* forms yellow needles and melts at  $242^{\circ}$ .

By the action of bromine on the base, a substance is obtained which crystallises in white needles, melts at  $117^{\circ}$ , and appears to be formed from the dibromide by loss of a mol. of hydrogen bromide.

6-Phenyl-o-nitro-2- $\beta$ -hydroxyphenethylpyridine,



the hydrochloride of which is formed from phenylmethylpyridine and o-nitrobenzaldehyde under slightly altered conditions, crystallises from dilute alcohol in white needles, sinters at  $65^{\circ}$ , and melts at  $95^{\circ}$ ; the *hydrochloride* forms short, yellow needles, dissolves fairly readily in water, and melts at  $182^{\circ}$ ; the *aurichloride* crystallises from dilute alcohol in yellow needles and melts at  $175^{\circ}$ ; the *platinichloride* forms orange-red needles, crystallises from dilute alcohol with  $2\text{H}_2\text{O}$ , and melts at  $156^{\circ}$ .

T. M. L.

*isoQuino- $\beta$ -pyridine*. By WILHELM MARCKWALD and H. DETTMER (*Ber.*, 1902, 35, 296—302).—3-Phenylpyridine-2:2'-dicarboxylic acid (Skraup and Cobenzl, *Abstr.*, 1883, 1010) yields its *anhydride* when dissolved in acetic anhydride at  $120^{\circ}$ ; the product separates from hot benzene in white crystals melting at  $183^{\circ}$ , and is converted by aqueous ammonia into 3-phenylpyridine-2:2'-dicarboxylamic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{C}_5\text{NH}_3\cdot\text{CO}\cdot\text{NH}_2$ , which forms white crystals, melts at  $200^{\circ}$ , and yields crystalline salts with both acids and alkalis; the *picrate*, melting at  $174^{\circ}$ , the *dichromate*, and the *silver* salt were analysed. The amide is converted by warm aqueous sodium hypobromite into

6-hydroxyisoquino- $\beta$ -pyridine, 
$$\begin{array}{c} \text{OH}\cdot\text{C}\cdot\text{N}-\text{C}-\text{N}=\text{CH} \\ | \quad | \quad | \\ \text{C}_6\text{H}_4\cdot\text{C}\cdot\text{CH}:\text{CH} \end{array}$$
 which crystallises

in white, felted needles, melts at  $274-276^{\circ}$  and sublimes at a higher temperature; the *picrate*, melting and decomposing at  $260^{\circ}$ , and the *platinichloride* were analysed. Its structure and that of the original amide follow from its yielding phthalic acid, not quinolinic acid, on oxidation.

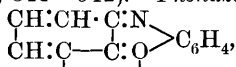
6-Chloroisoquino- $\beta$ -pyridine, obtained by heating the hydroxy-compound with phosphorus pentachloride and oxychloride for 4—5 hours at  $180^{\circ}$ , crystallises from toluene in yellowish-brown needles, melts at  $182-183^{\circ}$ , and yields a *picrate* decomposing at  $240^{\circ}$ ; when heated for 5 hours with concentrated hydriodic acid and phosphorus,

it is reduced to isoquino- $\beta$ -pyridine, 
$$\begin{array}{c} \text{CH}\cdot\text{N}\cdot\text{C}-\text{N}=\text{CH} \\ | \quad | \quad | \\ \text{C}_6\text{H}_4\cdot\text{C}\cdot\text{CH}:\text{CH} \end{array}$$
 which crystal-

lises from alcohol, melts at  $113-114^{\circ}$ , boils unchanged above  $360^{\circ}$ , and is a mono-acid base; the *hydrochloride*,  $\text{C}_{12}\text{H}_8\text{N}_2, \text{HCl}, 2\text{H}_2\text{O}$ , melts at first at  $99^{\circ}$ , or when anhydrous at  $207^{\circ}$ , the *picrate* melting at  $213^{\circ}$ , and the *dichromate* at  $170^{\circ}$ .

W. A. D.

The Simplest Azoxone. By FRIEDRICH KEHRMANN and A. SAAGER (*Ber.*, 1902, 35, 341—342).—Phenazoxone,



produced by oxidising phenoxazine with ferric chloride in glacial

acetic acid solution, crystallises from water in lustrous, yellowish-brown leaflets melting at 216—217°; it is only feebly basic, its salts being completely dissociated by water. The substance is insoluble in solutions of the alkali hydroxides, but dissolves in benzene or alcohol. G. T. M.

**Pyrazole Derivatives.** By EDUARD BUCHNER and CARL VON DER HEIDE (*Ber.*, 1902, 35, 31—34).—Methyl ethyl 4-phenylpyrazoline-3:5-dicarboxylate, produced by adding methyl diazoacetate to ethyl cinnamate, and its isomeride, obtained from ethyl diazoacetate and methyl cinnamate (Buchner and Dessauer, *Abstr.*, 1893, i, 282), when treated with bromine in chloroform solution, give rise to the same methyl ethyl 4-phenylpyrazole-3:5-dicarboxylate,  $\text{CPh} \begin{smallmatrix} \text{C}(\text{CO}_2\text{Et}) \cdot \text{N} \\ \text{C}(\text{CO}_2\text{Me}) \cdot \text{NH} \end{smallmatrix}$  or  $\text{CPh} \begin{smallmatrix} \text{C}(\text{CO}_2\text{Me}) \cdot \text{N} \\ \text{C}(\text{CO}_2\text{Et}) \cdot \text{NH} \end{smallmatrix}$ , this substance separating in rhombohedral crystals or needles melting at 105° and yielding 4-phenylpyrazole-3:5-dicarboxylic acid on hydrolysis with hydrochloric acid. The acid, when heated, loses carbon dioxide, giving rise to 4-phenylpyrazole. G. T. M.

**Pyrazole-4-carboxylic Acid from 4-Phenylpyrazole.** By WILHELM BEHAGHEL and EDUARD BUCHNER (*Ber.*, 1902, 35, 34—35).—Pyrazole-4-carboxylic acid (Buchner and Fritsch, *Abstr.*, 1893, i, 432) is produced in small amount from 4-phenylpyrazole by successively nitrating the base to a dinitro-derivative, reducing the product to the amine, and oxidising this with potassium permanganate solution; the acid is isolated from the products of oxidation in the form of its copper salt, this being subsequently decomposed by hydrogen sulphide; it decomposes at 275° and yields pyrazole by loss of carbon dioxide. G. T. M.

**Phenylacetylene and Alkyl Diazoacetates.** By EDUARD BUCHNER and LOUIS LEHMANN (*Ber.*, 1902, 35, 35—37).—Ethyl 5:3-phenylpyrazolecarboxylate, \*  $\text{C}_3\text{N}_2\text{H}_2\text{Ph} \cdot \text{CO}_2\text{Et}$ , obtained by heating together on the water-bath phenylacetylene and ethyl diazoacetate, separates from ether in colourless crystals and melts at 140°. The corresponding methyl ester produced from phenylacetylene and methyl diazoacetate melts at 181—182°. These esters, on hydrolysis, yield 5:3-phenylpyrazolecarboxylic acid, which melts at 233—234° (compare Knorr and Sjollemma, *Abstr.*, 1894, i, 546) and readily gives rise to 5-(or 3)-phenylpyrazole on heating at 140—150°. G. T. M.

**5:3-Pyrazolecarboxylic Acid from 5-(or 3)-Phenylpyrazole.** By EDUARD BUCHNER and CHRISTOPHOR HACHUMIAN (*Ber.*, 1902, 35, 37—42. Compare preceding abstract).—5-(or 3)-Phenylpyrazole is the only product of the action of hydrazine hydrate on benzoylaldehyde (Knorr, 1895, i, 395; von Rothenburg, 1895, i, 303), and is most readily prepared by this method.

\* It is uncertain which group is in the 3-, which in the 5-position.

5-(or 3-)*Nitrophenylpyrazole nitrate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_3\text{N}_2\text{H}_3, \text{HNO}_3$ , separates in yellow needles when 5-(or 3-)phenylpyrazole is added to cold fuming nitric acid; it decomposes at  $182-184^\circ$  and is decomposed on treatment with water or alkaline solutions into nitro-5-(or 3-)phenylpyrazole (Knorr, Abstr., 1894, i, 546).

5-(or 3-)*Dinitrophenylpyrazole*, obtained on nitrating 5-(or 3-)phenylpyrazole on the water-bath, forms colourless needles decomposing at  $212^\circ$ ; with solutions of the alkali hydroxides, it yields metallic derivatives, the *sodium* compound,  $\text{C}_9\text{H}_5\text{O}_4\text{N}_4\text{Na}$ , crystallising in lemon-yellow needles.

5-(or 3-)*Aminophenylpyrazole*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_3\text{H}_3\text{N}_2$ , resulting from the reduction of the nitro-compound with tin and hydrochloric acid, forms colourless needles melting at  $104^\circ$  and boiling at  $290-300^\circ$  under 12 mm. pressure; the *hydrochloride* and *sulphate* form colourless needles, the latter decomposing at  $242^\circ$ . The *platinichloride* separates in golden-yellow needles containing  $2\text{H}_2\text{O}$ ; it melts at  $105-110^\circ$ ; the *oxalate*,  $(\text{C}_9\text{H}_9\text{N}_3)_2\text{H}_2\text{C}_2\text{O}_4$ , with  $\text{H}_2\text{O}$ , melts at  $165^\circ$ , and the *picrate*, with  $1\frac{1}{2}\text{H}_2\text{O}$ , becomes anhydrous at  $110^\circ$ . 5-(or 3-)*Acetylaminophenylpyrazole*,  $\text{C}_9\text{H}_8\text{N}_3\text{Ac}$ , and the corresponding *benzoyl* derivative and the *thiocarbamide*,  $(\text{C}_9\text{H}_8\text{N}_3)_2\cdot\text{CS}$ , crystallise in colourless needles and melt respectively at  $207^\circ$ ,  $227^\circ$ , and  $200-202^\circ$ ; 5-(or 3-)*benzylideneaminophenylpyrazole*,  $\text{C}_9\text{H}_7\text{N}_3\cdot\text{CHPh}$ , is a white powder which melts somewhat indefinitely at  $65^\circ$  and is decomposed by water into its generators.

5-(or 3-)*Trimethylaminophenylpyrazole dimethiodide*,  $\text{C}_9\text{H}_6\text{N}_3\text{Me}_3 \cdot 2\text{MeI}$ , obtained by heating the base with methyl iodide at  $120^\circ$ , crystallises from methyl alcohol in colourless needles and melts at  $211^\circ$ .

5-(or 3-)*Tribromoaminophenylpyrazole*,  $\text{C}_9\text{H}_6\text{N}_3\text{Br}_3$ , produced by treating the base with bromine in ethereal solution, separates from this solvent in colourless needles and melts at  $207^\circ$ .

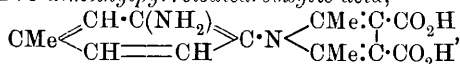
*Pyrazole-5-(or 3-)carboxylic acid*, prepared by oxidising 5-(or 3-)aminophenylpyrazole with a cold alkaline solution of permanganate, is separated in the form of its copper salt and isolated from this derivative by the action of hydrogen sulphide.

An oily phenylpyrazoline was stated to be formed by the action of hydrazine hydrate on cinnamaldehyde (Rothenburg, Abstr., 1894, i, 348; 1895, i, 302). On repeating this experiment, it was found that 5-(or 3-)phenylpyrazole was the only recognisable product.

G. T. M.

**Relative Difference in Basicity of the Two Amino-groups of Substituted Diamines.** By CARL BÜLOW and GEORG LIST (*Ber.*, 1902, 35, 185—192. Compare Abstr., 1900, i, 690; Tiemann, *Ber.*, 1870, 3, 221).—*o*-Tolylenediamine hydrochloride  $[\text{Me} : (\text{NH}_2)_2 = 1 : 3 : 4]$  and ethyl diacetylsuccinate readily react in alcohol-acetic acid solution, yielding *ethyl o-tolylene-bis-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate*,  $\text{C}_6\text{H}_3\text{Me}[\text{C}_4\text{NMe}_2(\text{CO}_2\text{Et})_2]_2$ , as a resinous product, which, on hydrolysis, yields the *tetracarboxylic acid* melting and decomposing at  $272^\circ$  and only very sparingly soluble in the usual organic solvents. The *acid silver* salt,  $\text{C}_{23}\text{H}_{20}\text{O}_8\text{N}_2\text{Ag}_2$ , has been prepared. The amount of alkali required to neutralise the acid, using phenolphthalein as indicator, corresponds with a di- and not with a tetra-basic acid.

*Aminotolyl-2 : 5-dimethylpyrroledicarboxylic acid,*



is formed when molecular proportions of *o*-tolylenediamine hydrochloride and ethyl diacetylsuccinate are boiled for half-an-hour in an alcohol-acetic acid solution, and the resulting ester hydrolysed. It crystallises from alcohol in small needles, melts and decomposes at 205°, and is only sparingly soluble in the usual solvents. An *acid ammonium* and an *acid silver* salt have been prepared. The constitution of the acid has been established by the removal of the amino-group and conversion of the acid into Knorr's *p*-tolyl-2 : 5-dimethylpyrrole-3 : 4-dicarboxylic acid (Abstr., 1885, 555).

It would thus appear that the amino-group in the *para*-position to the methyl group is the more strongly basic of the two amino-groups in *o*-tolylenediamine [ $\text{Me} : (\text{NH}_2)_2 = 1 : 3 : 4$ ]. J. J. S.

**Derivatives of Toluene-*p*-sulphonic Chloride and *o*-Nitrotoluene-*p*-Sulphonic Chloride.** By FRÉDÉRIC REVERDIN and PIERRE CRÉPIEUX (*Ber.*, 1902, 35, 314—315. Compare Abstr., 1901, i, 686).—*Bis-toluene-p-sulphon-o-phenylenediamide*,  $\text{C}_6\text{H}_4(\text{NH} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4\text{Me})_2$ , obtained by boiling together toluene-*p*-sulphonic chloride and *o*-phenylenediamine in alcoholic solution, crystallises from this solvent in white needles and melts at 201—202°.

*Bis-o-nitrotoluene-p-sulphon-o-phenylenediamide*,  $\text{C}_6\text{H}_4(\text{NH} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NO}_2)_2$ , prepared from *o*-nitrotoluene-*p*-sulphonic chloride and *o*-phenylenediamine, crystallises from dilute acetic acid in white needles melting at 162—163°; like the preceding compound, this substance is readily soluble in all the ordinary solvents excepting light petroleum.

*Bis-toluene-p-sulphon-m-phenylenediamide*, produced by condensing its generators in pyridine solution, crystallises from dilute acetic acid or alcohol in white needles melting at 172°; it is hydrolysed by cold concentrated sulphuric acid.

*Bis-o-nitrotoluene-p-sulphon-p-phenylenediamide*, obtained by the method employed for preparing its isomerides, crystallises from acetone in pale yellow prisms melting above 250°; it readily dissolves in hot acetone, but is sparingly soluble in the other organic solvents. G. T. M.

**Complex Cyclic Systems containing Nitrogen.** By OSCAR HINSBERG (*Annalen*, 1901, 319, 257—286).—Systems of conjugated six-membered rings, arranged with their centres in a straight line, are indicated by the prefix "*lin*" (linear), those interlinked in such a manner that more than two of their centres never lie in the same straight line are denoted by the prefix "*ang*" (angular), whilst the double prefix "*lin-ang*" is employed for compounds exhibiting both forms of conjugation.

*Lin-dihydronaphthaphenazine* (dihydro- $\beta_1\beta_2$ -naphthaphenazine), obtained from 2 : 3-dihydroxynaphthalene and *o*-phenylenediamine, readily yields its azine when oxidised with potassium dichromate and acetic acid; the reverse change is readily effected by the action of stannous chloride or alcoholic ammonium sulphide. The azine yields



a compound with benzenesulphinic acid and reacts with aniline, giving rise to *anilino- $\beta_1\beta_2$ -naphthaphenazine*,  $\text{NHPh}\cdot\text{C}_{16}\text{H}_9\text{N}_2$ , a change involving simultaneous addition of the amine and oxidation.

*lin-ang-Dihydronaphthazine* ( $\alpha_1\beta_1\beta_1'\beta_2'$ -dihydronaphthazine), obtained from 2:3-dihydroxynaphthalene and 1:2-naphthylenediamine, readily yields its azine on oxidation with dichromate and acetic acid, the latter base melting at 246–247°, and not at 240° (Fischer and Albert, Abstr., 1896, i, 701).

*lin-Dihydronaphthazine* ( $\beta_1\beta_2\beta_1'\beta_2'$ -dihydronaphthazine), produced by heating together 2:3-dihydroxynaphthalene and 2:3-naphthylenediamine in a current of carbon dioxide at 180°, is obtained as a yellow, crystalline powder and does not melt below 300°. All attempts to oxidise this dihydro-base to the corresponding azine were fruitless.

Fluoflavine, formed from 2:3-dichloroquinoxaline and *o*-phenylenediamine has already been shown to be easily oxidised to quinoxalophenazine (Abstr., 1896, i, 394). The reverse change is very readily effected by the action of reducing agents, such as ammonium sulphide, stannous chloride, sulphurous acid, and quinol. The double azine is readily converted into chlorofluoflavine and phenylfluoflavylsulphone by the action of hydrochloric acid and benzenesulphinic acid respectively, the sulphone being oxidised by chromic acid mixture to the sulphone of the double azine.

*lin-ang-Naphthafluoflavine* ( $\alpha\beta$ -naphthafluoflavine) results from the condensation of 2:3-dichloroquinoxaline with 1:2-naphthylenediamine at 140–160°; it crystallises in yellow needles and melts above 300°.

*lin-ang-Quinoxalonaphthazine* (*quinoxalo- $\alpha\beta$ -naphthazine*), obtained by oxidising the preceding compound, crystallises in blood-red leaflets and decomposes at 290°. The reverse change is effected by the ordinary reducing agents, excepting quinol in alcoholic solution; this azine is accordingly less reactive than quinoxalophenazine.

*lin-ang-Chloronaphthafluoflavine*,  $\text{C}_{18}\text{H}_{11}\text{N}_4\text{Cl}$ , produced by mixing the preceding double azine with concentrated hydrochloric acid, separates from glacial acetic acid in yellow needles and melts above 300°.

*lin-Naphthafluoflavine* ( $\beta_1\beta_2$ -naphthafluoflavine), prepared by melting together at 130–150° 2:3-dichloroquinoxalone and 2:3-naphthylenediamine, crystallises from glacial acetic acid in yellow needles and melts above 300°; it is sparingly soluble in alcohol or benzene and yields a potassium derivative on treatment with alcoholic potassium hydroxide. It is not possible to convert this substance into the corresponding double azine by oxidation with chromic acid.

From these experimental results, the following conclusions are deduced. The stability of the azines and double azines diminishes as the number of linearly conjugated rings increases, the compounds of this type with five linearly arranged rings being incapable of existence; conversely, the stability of the dihydrogenised nitrogen compounds increases with the number of the linearly attached rings.

The *ang*-compounds are more stable than their *lin*-isomerides. The addition to a linear system of one or more rings angularly disposed increases its stability.

The remainder of the communication is devoted to a discussion of

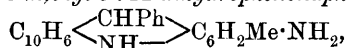
the application of these principles to other cases of conjugated ring systems.

G. T. M.

**Derivatives of Phenyl[pheno]naphthacridine.** By FRITZ ULLMANN, N. A. RACOVITZA, and MELANIE ROZENBAND (*Ber.*, 1902, 35, 316—325. Compare *Abstr.*, 1900, i, 360, 361, 689).—5-Phenyl-3-methylphenonaphthacridine (compare this vol., i, 55) yields a *hydrochloride* crystallising in yellow needles which are decomposed by water; the *platinichloride* is a yellow, crystalline, insoluble substance.

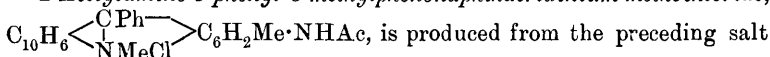
*p*-Nitrobenzylidene-*p*-toluidine behaves unlike its isomeride, *m*-nitrobenzylidene-*p*-toluidine, when condensed with  $\beta$ -naphthol, and yields chiefly *p*-nitrobenzylidene- $\beta$ -dinaphthyl oxide,  $\text{O} \left\langle \begin{smallmatrix} \text{C}_{10}\text{H}_6 \\ \text{C}_{10}\text{H}_6 \end{smallmatrix} \right\rangle \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , and only a trace of an acridine derivative (this vol., i, 56).

2-Amino-5-phenyl-3-methyl-5:12-dihydrophenonaphthacridine,



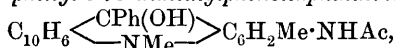
produced by condensing  $\beta$ -naphthol either with benzylidene-*m*-tolylene-diamine or the corresponding tetra-aminoditolylphenylmethane, separates from aniline in white crystals melting indefinitely at  $271^\circ$ ; on oxidation with ferric chloride, it yields the hydrochloride of the corresponding acridine (this vol., i, 56), this salt separating from dilute acetic acid in red leaflets. The acetyl derivative of 2-amino-3-methyl-5-phenylphenonaphthacridine, when treated with dimethyl sulphate in nitrobenzene solution, gives rise to the corresponding acridinium methyl sulphate, which separates in yellow crystals.

2-Acetyl-amino-5-phenyl-3-methylphenonaphthacridinium methochloride,



is produced from the preceding salt by double decomposition with sodium chloride, and separates in orange-yellow crystals; the *platinichloride* and *dichromate* are yellow and red crystalline precipitates respectively.

2-Acetyl-amino-5-phenyl-3:5-dimethylphenonaphthacridol,



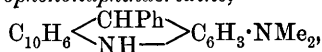
obtained by treating the methochloride with alcoholic ammonia, crystallises from xylene in pale pink coloured leaflets melting and decomposing at  $210^\circ$ .

2-Amino-5-phenyl-3-methylphenonaphthacridinium methochloride, resulting from the hydrolysis of the corresponding acetyl derivative, crystallises in red needles soluble in hot water. The corresponding *nitrate* is prepared by mixing 2-amino-5-phenyl-3-methylphenonaphthacridine with dimethyl sulphate in nitrobenzene solution, and treating the residue, after distillation, in steam with nitric acid; it separates in red crystals sparingly soluble in water; the *platinichloride* is an orange-coloured, crystalline substance; the *dichromate* is a dark-red insoluble powder.

G. T. M.

**2-Alkylamino-5-phenylphenonaphthacridines.** By FRITZ ULLMANN, MELANIE ROZENBAND, BENNO MÜHLHAUSER, and E. GREYER (*Ber.*, 1902, 35, 326—340. Compare preceding abstract).—2-Dimethyl-

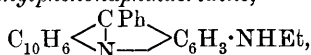
*amino-5-phenyldihydrophenonaphthacridine*,



produced by condensing together a mixture of *m*-aminodimethylaniline, benzaldehyde, and  $\beta$ -naphthol, separates from benzene as an almost colourless, crystalline powder melting at  $230^\circ$ .

*2-Dimethylamino-5-phenylnaphthacridine* is obtained by oxidising the preceding compound either with atmospheric oxygen or ferric chloride; the base forms orange-yellow needles and melts at  $216^\circ$ ; its *hydrochloride* crystallises from dilute acetic acid in brick-red needles; the *dichromate* is a red, insoluble powder.

*2-Ethylamino-5-phenylphenonaphthacridine*,



prepared from *m*-aminoethylaniline, separates in yellowish-brown crystals and melts at  $220-221^\circ$ .

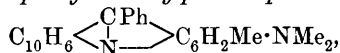
*2-Methylamino-5-phenyl-3-methyldihydrophenonaphthacridine*, obtained by condensing 4-aminomethyl-*o*-toluidine with benzaldehyde and  $\beta$ -naphthol, is a white, crystalline powder melting at  $247^\circ$ , and dissolving in benzene to a solution exhibiting a blue fluorescence.

The corresponding *acridine* base,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{CPh} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{C}_6\text{H}_2\text{Me} \cdot \text{NHMe}$ , prepared from the preceding compound by the action of alcoholic ferric chloride, crystallises from benzene in yellow leaflets melting at  $270^\circ$ ; its solutions are yellow and exhibit a green fluorescence; the *hydrochloride* forms orange-yellow needles sparingly soluble in boiling water.

4-Aminoethyl-*o*-toluidine, when condensed in a similar manner, yields *2-ethylamino-5-phenyl-3-methyldihydrophenonaphthacridine*, a pale yellow, crystalline powder melting at  $227^\circ$ , which, on oxidation, gives

rise to the corresponding *acridine*,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{CPh} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{C}_6\text{H}_2\text{Me} \cdot \text{NHEt}$ , a base forming yellow needles and melting at  $258^\circ$ ; the *hydrochloride* separates in lustrous, red needles; the *nitrate* is obtained in light red, lustrous leaflets sparingly soluble in water, but more so in alcohol.

*2-Dimethylamino-5-phenyl-3-methylphenonaphthacridine*,



and its *dihydro*-compound, produced from aminodimethyl-*o*-toluidine by the condensation previously indicated, separate respectively in orange-red needles and white, crystalline granules, the corresponding melting points being  $210^\circ$  and  $238^\circ$ ; the *hydrochloride* and the *nitrate* of the former base form lustrous, red needles and scarlet leaflets respectively.

4-Nitrodiethyl-*o*-toluidine, produced by nitrating diethyl-*o*-toluidine, is a reddish oil, boiling with slight decomposition at  $295-297^\circ$  under 727.5 mm. pressure; on reduction, it yields 4-aminodiethyl-*o*-toluidine, an oil boiling at  $265-266^\circ$  under 730 mm. pressure. The diamine, on condensation, gives rise to *2-diethylamino-5-phenyl-3-methyldihydrophenonaphthacridine*, a substance obtained as a white, crystalline powder melting at  $186^\circ$ , and this in turn yields the *phenonaphthacridine*,

$\text{C}_{10}\text{H}_6 \begin{array}{c} \text{CPh} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{C}_6\text{H}_2\text{Me} \cdot \text{NEt}_2$ , a base crystallising in yellow needles

and melting at 200—201°, the *hydrobromide* of which separates from dilute alcohol in lustrous, red leaflets.

4-*Nitrobenzyl-o-toluidine*, prepared by heating 4-nitro-*o*-toluidine with benzyl chloride in nitrobenzene solution, crystallises from alcohol, benzene, or glacial acetic acid in yellow leaflets melting at 124°; on reduction, it gives rise to 4-*aminobenzyl-o-toluidine*, a diamine crystallising in colourless, silky needles and melting at 81°.

2-*Benzylamino 5-phenyl-3-methylphenonaphthacridine* results from the simultaneous condensation and oxidation of the preceding base with benzaldehyde and  $\beta$ -naphthol; it crystallises in pale yellow needles, melts at 302°, and is somewhat sparingly soluble in the organic solvents of low boiling point. The *hydrochloride* and *hydrobromide* of this acridine separate in thick, dark-red prisms or needles.

The hydrochlorides of the preceding acridine derivatives dye wool mordanted with tannic acid from a dilute acetic acid bath.

G. T. M.

**Constitution of Phenylurazole.** By S. F. ACREE (*Ber.*, 1902, 35, 553—562. Compare Pinner, *Abstr.*, 1887, 1043; 1888, 687).—*Ethyl phenylsemicarbazidedicarboxylate*,  $\text{CO}_2\text{Et}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , obtained by the action of ethyl chlorocarbonate on phenylsemicarbazide, exists in two crystalline modifications melting at 172° and at 154°, and, when warmed with excess of sodium hydroxide, is converted into phenylurazole. A study of the properties of the latter substance indicate that it is probably 3-*hydroxy-5-keto-1-phenyl-2:5-dihydrotriazole*,

$\text{NPh}\cdot\text{NH}$   
|  
 $\text{CO}-\text{N} \Rightarrow \text{C}\cdot\text{OH}$ . When titrated with sodium hydroxide, using phenolphthalein as indicator, it behaves as a strong monobasic acid. The *silver* derivative forms a white precipitate decomposing at 252° and soluble in ammonia; the *barium* derivative,  $(\text{C}_8\text{H}_6\text{O}_2\text{N}_3)_2\text{Ba}\cdot 2\text{H}_2\text{O}$ , crystallises in plates decomposing at 280—300°. When phenylurazole is warmed with methyl iodide and alcoholic potash, it is converted into Busch and Heinrichs' 3-*hydroxy-5-keto-1-phenyl-2-methyl-2:5-dihydrotriazole* (*Abstr.*, 1900, i, 314) melting at 183°. The same derivative is obtained when silver phenylurazole is boiled with alcoholic methyl iodide solution. It is a monobasic acid, yields a *silver* salt,  $\text{C}_9\text{H}_5\text{O}_2\text{N}_3\text{Ag}$ , and is not decomposed when evaporated to dryness with concentrated hydrochloric acid, hence the methyl group is presumably attached to nitrogen. The isomeric 3-*hydroxy-5-keto-1-phenyl-4-methyl-*

4:5-*dihydrotriazole*,  $\text{NPh}-\text{N}$   
|  
 $\text{CO}-\text{NMe} \Rightarrow \text{C}\cdot\text{OH}$ , may be obtained from phenylsemicarbazide and methylacetylcarbamide; it melts at 225°, gives a violet coloration with alcoholic ferric chloride, and yields mono-*sodium* and *silver* derivatives, the latter decomposing at 225°.

3-*Ethoxy-5-keto-1-phenyl-2:5-dihydrotriazole*, obtained by the action of ethyl iodide, in the cold, on a mixture of benzene and silver phenylurazole, is a crystalline solid melting at about 141° (?) and readily soluble in ether, benzene, or alcohol, but insoluble in alkalis. It is readily hydrolysed when warmed with alcoholic hydrochloric acid, and is isomeric with Wheeler's 5-*hydroxy-3-ethoxy-1-phenyltriazole* (*Abstr.*, 1900, i, 563).

3-Acetoxy-5-keto-1-phenyl-2 : 5-dihydrotriazole is an oil, and is readily oxidised by acids or alkalis.

Diphenylurazine (Pinner, *loc. cit.*, and Heller, *Annalen*, 1891, 263, 382) is a monobasic acid, yields a mono-silver salt, and from Rupe and Labhardt's researches (Abstr., 1899, i, 356) appears to have the formula  $\text{CO} \begin{smallmatrix} \text{NPh} - \text{N} \\ \text{NPh} \cdot \text{NH} \end{smallmatrix} \text{C} \cdot \text{OH}$ , and not the symmetrical constitution suggested by Pinner.

When warmed with alkali, it is not transformed into an isomeride melting at 231° as stated by Pinner. J. J. S.

**Synthesis of Aryl Leucauramines.** By RICHARD MÖHLAU and M. HEINZE (*Ber.*, 1902, 35, 358—375. Compare this vol., i, 63).—Arylamines readily react with tetramethyldiaminobenzhydrol, forming leucauramines with elimination of water, whilst aliphatic amines are not capable of interacting with the hydrol; similarly, arylamines and ordinary leucauramine yield substituted leucauramines and ammonia.

For the preparation of the benzhydrol, the authors recommend the oxidation of tetramethyldiaminodiphenylmethane hydrochloride in dilute aqueous solution by lead dioxide and acetic acid—a method which produces besides the hydrol a certain amount of hydrol-anhydride (see below). The reduction of Michler's ketone, by Michler and Dupertuis's method, also gives very good results.

*Tetramethyldiaminodiphenylmethyl oxide*,  $\text{O}[\text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2]_2$ , is formed when the hydrol is heated at 100°, and is distinguished from the latter by its insolubility in ether; it crystallises in colourless, rhombic prisms, melting at 195°, and when heated with acids is reconverted into the hydrol.

*Phenyl-leucauramine*,  $\text{NHPh} \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , prepared by heating molecular proportions of aniline and tetramethyldiaminobenzhydrol in alcoholic solution at 100°, or from aniline and leucauramine, or by reduction of phenylauramine by means of sodium amalgam, crystallises from benzene in colourless prisms melting at 154°. Although it dissolves in concentrated acids, forming a colourless solution, it is immediately decomposed by dilute acids into aniline and the benzhydrol. *o-Tolyl-leucauramine*,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , prepared in a similar manner from the benzhydrol and *o*-toluidine, forms colourless prisms melting at 133°; the *p*-tolyl derivative crystallises in colourless prisms melting at 150°, and unlike the ortho-derivative may be boiled with alcohol without undergoing decomposition. *m*-Toluidine does not react with the benzhydrol. *m-Xylol-leucauramine*,  $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{NH} \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , prepared from *m*-xylylidine and the benzhydrol, crystallises in colourless prisms melting at 147°.

*Anilino-leucauramine*,  $\text{NHPh} \cdot \text{NH} \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , prepared from phenylhydrazine and the benzhydrol or from phenylhydrazine and leucauramine, forms colourless prisms melting at 116°. This substance could not be obtained by reduction of the phenylhydrazone of tetramethyldiaminobenzophenone (prepared by heating auramine hydrochloride and phenylhydrazine at 160°); with zinc dust and sodium hydroxide, the latter yielded *tetramethyldiaminodiphenylmethylimine*,  $\text{NH}[\text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2]_2$ , which melts at 135°.

*α-Naphthyl-leucauramine*,  $C_{10}H_7 \cdot NH \cdot CH(C_6H_4 \cdot NMe_2)_2$ , prepared from *α*-naphthylamine and the benzhydrol, crystallises in colourless, prismatic needles melting at  $182^\circ$ ; the *β*-naphthyl derivative forms colourless prisms melting at  $191^\circ$ .

*o-Nitrophenyl-leucauramine*,  $NO_2 \cdot C_6H_4 \cdot NH \cdot CH(C_6H_4 \cdot NMe_2)_2$ , prepared from *o*-nitroaniline and the benzhydrol, crystallises in golden-yellow, prismatic needles melting at  $164^\circ$ ; the *m*-nitro-derivative in golden-yellow prisms melting at  $152^\circ$ ; and the *p*-nitro-derivative in lemon-yellow prisms melting at  $186^\circ$ ; the last-mentioned substance is far more stable towards boiling alcohol than the two former. *p-Ethoxyphenyl-leucauramine*,  $OEt \cdot C_6H_4 \cdot NH \cdot CH(C_6H_4 \cdot NMe_2)_2$ , prepared from *p*-phenetidine and the benzhydrol, forms prisms melting at  $159$ – $160^\circ$ .

*Phenylene-p-dileucauramine*,  $C_6H_4[NH \cdot CH(C_6H_4 \cdot NMe_2)_2]_2$ , prepared by boiling *p*-phenylenediamine (1 mol.) and the benzhydrol (2 mols.) in alcoholic solution, crystallises in colourless prisms melting at  $225^\circ$ ; the analogous compound, obtained by using *m*-phenylenediamine, melts at  $247$ – $248^\circ$ , and is far more stable towards acids than the other leucauramines, yielding with dry hydrogen chloride a hydrochloride which forms colourless leaflets.

*m-Amino-p-tolyl-leucauramine*,  $NH_2 \cdot C_6H_3Me \cdot NH \cdot CH(C_6H_4 \cdot NMe_2)_2$  [Me:  $NH_2$ :  $NH$  = 1 : 3 : 4], prepared from tolylene-3:4-diamine and the benzhydrol, forms prismatic crystals melting at  $165^\circ$ . *o-Amino-p-tolyl-leucauramine*,  $NH_2 \cdot C_6H_3Me \cdot NH \cdot CH(C_6H_4 \cdot NMe_2)_2$  [Me:  $NH_2$ :  $NH$  = 1 : 2 : 4], obtained by using tolylene-2:4-diamine, crystallises in colourless crystals melting at  $209^\circ$ .

*Diphenylene-4:4'-dileucauramine*,  $C_{12}H_8[NH \cdot CH(C_6H_4 \cdot NMe_2)_2]_2$ , prepared from benzidine and the benzhydrol, crystallises in colourless prisms melting at  $242$ – $243^\circ$ . *3:3'-Dimethyldiphenylene-4:4'-dileucauramine*,  $C_{12}H_6Me_2[NH \cdot CH(C_6H_4 \cdot NMe_2)_2]_2$ , forms colourless, lustrous prisms melting at  $229$ – $230^\circ$ .

*Dianisylene-4:4'-dileucauramine*,  $C_{12}H_6(OMe)_2[NH \cdot CH(C_6H_4 \cdot NMe_2)_2]_2$ , crystallises in colourless prisms with a silky lustre melting at  $259$ – $260^\circ$ .

*o-Leucauraminobenzoic acid*,  $CH(C_6H_4 \cdot NMe_2)_2 \cdot NH \cdot C_6H_4 \cdot CO_2H$ , prepared from *o*-aminobenzoic acid and the benzhydrol, crystallises in colourless prisms melting at  $153^\circ$ ; the corresponding *p*-derivative forms prisms melting at  $192$ – $193^\circ$ ; its sodium salt crystallises in leaflets. *m*-Aminobenzoic acid does not react with the benzhydrol.

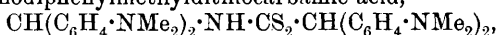
Carbamide readily condenses with the benzhydrol, yielding *carbonyl-dileucauramine*,  $CO[NH \cdot CH(C_6H_4 \cdot NMe_2)_2]_2$ , which crystallises in star-shaped aggregates of colourless prisms melting at  $250$ – $251$ ; the hydrochloride forms leaflets.

K. J. P. O.

**New Reactions of Leucauramines.** By RICHARD MÖHLAU, M. HEINZE, and R. ZIMMERMANN (*Ber.*, 1902, **35**, 375–383. Compare preceding abstract).—Although auramine is readily converted into leucauramine by reduction of an alcoholic solution with sodium amalgam (Graebe, *Abstr.*, 1888, i, 158), reduction of the alkaline alcoholic solution with zinc dust leads to the formation of tetramethyldiaminodiphenylmethyline (m. p.  $185^\circ$ , Weil, *Abstr.*, 1894, i, 419). The latter compound is also formed when the benzhydrol is heated with

leucauramine in alcoholic solution, or when leucauramine is heated at its melting point. By heating leucauramine and sulphur, together at  $140^{\circ}$ , tetramethyldiaminothiobenzophenone (m. p.  $202^{\circ}$ , Fehrmann, Abstr., 1888, i, 156, and Wallach, Abstr., 1891, i, 189) is produced. When hydrogen sulphide is passed into an alcoholic solution of leucauramine, *tetramethyldiaminodiphenylmethyl sulphide*,  $S[CH(C_6H_4 \cdot NMe_2)_2]_2$ , is formed, crystallising in rhombic plates melting at  $172^{\circ}$ ; it is also obtained when aryl-leucauramines are treated with hydrogen sulphide, and when leucauramine and aryl-leucauramines are acted on by ammonium sulphide,  $(NH_4)_2S$ . With ammonium polysulphide,  $(NH_4)_2S_2$ , the aryl-leucauramines yield *tetramethyldiaminodiphenylmethyl disulphide*,  $S_2[CH(C_6H_4 \cdot NMe_2)_2]_2$ , which crystallises in star-like aggregates of prisms melting at  $207^{\circ}$ .

Carbon disulphide and leucauramine readily condense to the *leucauramine* salt of tetramethyldiaminodiphenylmethyldithiocarbamic acid,  $CH(C_6H_4 \cdot NMe_2)_2 \cdot NH \cdot CS \cdot S \cdot NH_3 \cdot CH(C_6H_4 \cdot NMe_2)_2$ , which forms colourless crystals melting at  $167^{\circ}$ . When warmed with alcohol, ammonia is evolved, and the *tetramethyldiaminodiphenylmethyl ester* of tetramethyldiaminodiphenylmethyldithiocarbamic acid,



which crystallises in thin, colourless needles melting at  $168^{\circ}$ . When heated under pressure, carbon disulphide and leucauramine yield tetramethyldiaminodiphenylmethyl sulphide. The aryl-leucauramines and carbon disulphide give phenylthiocarbimide and tetramethyldiaminodiphenylmethyl disulphide.

Tetramethyldiaminothiobenzhydrol (D.R.-P., 58198) does not condense with aromatic bases, and readily breaks up into hydrogen sulphide and the sulphide previously described. K. J. P. O.

**Action of Semicarbazide on Benzil.** By HEINRICH BILTZ and THANKMAR ARND (*Ber.*, 1902, 35, 344—347. Compare Posner, this vol., i, 82).—Benzilmonosemicarbazone is obtained, even at the ordinary temperature, on adding potassium acetate to an alcoholic solution of benzil and semicarbazide hydrochloride; it crystallises in colourless, octagonal plates and melts at  $174$ — $175^{\circ}$ . The supposed isomeride of this compound indicated by Posner is in reality 5:6-diphenyl-3-oxy-1:2:4-triazine formerly described by Thiele and Stange.

*Benzildisemicarbazone*,  $C_6Ph_2(N \cdot NH \cdot CO \cdot NH_2)_2$ , prepared by boiling semicarbazide hydrochloride, benzil, and potassium acetate in dilute alcohol for 8 hours, crystallises from alcohol or pyridine in thin leaflets melting at  $243$ — $244^{\circ}$ ; it is accompanied by 5:6-diphenyloxotriazine, being separated from this substance by fractional crystallisation from alcohol.

Both these carbazones are readily hydrolysed by concentrated hydrochloric acid. G. T. M.

**Action of Hypophosphorous Acid on Diazo-compounds.** By JULIUS MAI (*Ber.*, 1902, 35, 162—163).—The use of cuprous hydride in Sandmeyer's reaction was first tested, but it was found that diazo-salts were readily converted into hydrocarbons by the action of the hypophosphorous acid used in its preparation; for example, a 60 per

cent. yield of diphenyl is obtained by the diazotisation of benzidine and subsequent treatment with hypophosphorous acid. R. H. P.

**Esters of Nitronic Acids** [*iso*Nitro-compounds] and **Arylazoaldoximes**. By EUGEN BAMBERGER (*Ber.*, 1902, 35, 54—66). —The name "nitronic acid" is suggested for substances containing the group  $>\text{C}:\text{NO}\cdot\text{OH}$ , instead of the name "*isonitro*-compound" at present in use.

Methyl phenylazoethylidenenitronate  $\text{NPh}\cdot\text{N}\cdot\text{CMe}\cdot\text{NO}_2\text{Me}$ , is formed from diazomethane and phenylazonitroethane (nitroacetaldehyde phenylhydrazone,  $\text{NHPh}\cdot\text{N}\cdot\text{CMe}\cdot\text{NO}_2$ , the product of the action of nitroethane and diazobenzene, V. Meyer, this Journ., 1875, 1202. The constitution follows from the fact that, with dilute hydrochloric acid, benzene-diazonium chloride is formed, and that with an acetic acid solution of  $\alpha$ -naphthylamine the ester gives an intense coloration, characteristic of the phenylazo-group. Further, this ester, which is very unstable, as are all derivatives of nitronic acids, is decomposed when heated with water into formaldehyde and an acidic substance which proved to be phenylazoacetaldoxime,  $\text{NPh}\cdot\text{N}\cdot\text{CMe}\cdot\text{NOH}$  (compare Seidel, Abstr., 1892, 1417, and Nef, Abstr., 1895, i, 3, on the decomposition of ethyl fulminurate, &c.); the latter forms a monobenzoyl derivative and with dilute hydrochloric acid yields hydroxylamine, diazobenzene, and acetaldehyde (which is oxidised to acetic acid); further, it is produced by reduction of nitroacetaldehyde phenylhydrazone in alkaline solution to phenylhydrazoacetaldoxime,  $\text{NHPh}\cdot\text{NH}\cdot\text{CMe}\cdot\text{NOH}$ , and subsequent oxidation of the latter by ferric chloride, and by the interaction of alkyl nitrites and acetaldehyde phenylhydrazone in the presence of sodium ethoxide, reactions which are generally applicable to the synthesis of arylazoaldoximes.

The arylazoaldoximes are all yellow, well crystallised substances, soluble in alkalis and easily reduced to arylhydrazoaldoximes. With concentrated hydrochloric acid, phenylazoacetaldoxime yields *p*-chlorophenylhydrazoacetaldoxime,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}_2\text{H}_2\cdot\text{CMe}\cdot\text{NOH}$ ; this was also synthesised from *p*-chlorodiazobenzene and nitroethane, the nitroacetaldehyde *p*-chlorophenylhydrazone thus obtained yielding, on reduction, the hydrazoaldoxime.

The reaction of hydrochloric acid and phenylazoacetaldoxime is represented thus: there is first formed an additive product, a chlorohydrazoacetaldoxime,  $\text{NPhCl}\cdot\text{NH}\cdot\text{CMe}\cdot\text{NOH}$ , which in the presence of hydrochloric acid undergoes an intramolecular transformation, the chlorine taking the place of the hydrogen atom in the para-position in the benzene nucleus relative to the nitrogen atom. *p*-Chlorophenylazoacetaldoxime, prepared by oxidation of the hydrazo-compound with hydrochloric acid, gives 2:4-dichlorophenylhydrazoacetaldoxime, and the azo-compound obtained from this with hydrochloric acid similarly yields 2:4:6-trichlorophenylhydrazoacetaldoxime. 2:4:6-Trichlorophenylazoacetaldoxime reacts with hydrogen chloride in ethereal solution, yielding 2:4:6-trichlorophenylhydrazoacetaldoxime, *s*-trichlorobenzene, acethydroxamic acid, and nitrogen; the chlorohydrazo-derivative first formed reacts with the excess of hydrogen chloride, giving chlorine and the hydrazo-compound; the chlorine thus set free converts part of the



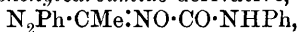
azo-compound into chloroacethydroxamic acid and trichlorodiazonium chloride; these substances respectively are converted into acet-hydroxamic acid and trichlorobenzene and nitrogen.

In the Griess reaction of diazonium salts with alcohol, the author sees an analogy with the decomposition of alkylphenylazoethylidene-nitronate with water into an aldehyde and phenylazoacetaldoxime; the diazonium ether,  $\text{N}:\text{NPh}\cdot\text{OEt}$ , first formed, is, on the one hand, transformed into the diazo-ether,  $\text{NPh}\cdot\text{N}\cdot\text{OEt}$ , which yields phenyl ethyl ether and nitrogen, on the other hand decomposed into acetaldehyde and phenylazohydride,  $\text{NPh}\cdot\text{NH}$ , which is immediately converted into benzene and nitrogen.

K. J. P. O.

**Ester of Phenylazoethylidenenitronic Acid and Phenylazo-acetaldoxime.** By EUGEN BAMBERGER and JAC. GROB (*Ber.*, 1902, 35, 67—82. Compare preceding abstract).—*Methyl phenylazoethylidenenitronate*,  $\text{N}_2\text{Ph}\cdot\text{CMe}\cdot\text{NO}_2\text{Me}$ , is prepared by adding diazomethane to an ethereal solution of nitroacetaldehyde phenylhydrazone, and crystallises in dark ruby-red, rhombic pyramids melting at  $71.5\text{--}72^\circ$ ; in this reaction, there is also formed a small quantity of a substance crystallising in yellow needles melting at  $95.5\text{--}96^\circ$ . The ester is extremely unstable and decomposes rapidly into phenylazoacetaldoxime and formaldehyde; on reduction with stannous chloride, phenylhydrazo-acetaldoxime is obtained.

*Phenylazoacetaldoxime*,  $\text{N}_2\text{Ph}\cdot\text{CMe}\cdot\text{NOH}$ , is prepared by boiling the substance just described with water, and crystallises in orange-yellow, monoclinic needles melting at  $117\text{--}118^\circ$ , and readily soluble in alkalis. Concentrated sulphuric acid dissolves the oxime with a red coloration, which, on addition of water, becomes first blue and finally orange-yellow. When warmed with hydrochloric acid, it decomposes into acetaldehyde, benzenediazonium chloride, and hydroxylamine, the two former appearing respectively as acetic acid and phenol. *Benzoyl-phenylazoacetaldoxime*,  $\text{N}_2\text{Ph}\cdot\text{CMe}\cdot\text{NOBz}$ , prepared by the Schotten-Baumann method, crystallises in pale yellow, flattened needles melting at  $137\text{--}137.5^\circ$ ; the *phenylcarbamide* derivative,



prepared by the action of phenylcarbimide, crystallises in orange-red, lustrous needles melting at  $123.5\text{--}124^\circ$ .

*Phenylhydrazoacetaldoxime*,  $\text{N}_2\text{H}_2\text{Ph}\cdot\text{CMe}\cdot\text{NOH}$ , is prepared by reducing phenylazoacetaldoxime by an alcoholic solution of ammonium sulphide, and crystallises in white needles or leaflets melting at  $128^\circ$ ; the base is very readily oxidised to the azo-oxime,—an operation which is best effected by ferric chloride.

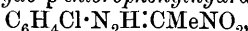
On treating phenylazoacetaldoxime with concentrated hydrochloric acid, it is immediately converted into *p-chlorophenylhydrazoacetaldoxime hydrochloride*,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}_2\text{H}_2\cdot\text{CMe}\cdot\text{NOH}\cdot\text{HCl}$ , which crystallises in needles melting and decomposing at  $169^\circ$ ; the *base*, obtained from the hydrochloride, crystallises in white needles with a silky lustre melting and decomposing at  $129^\circ$ . *p-Chlorophenylazoacetaldoxime*,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}_2\cdot\text{CMe}\cdot\text{NOH}$ , prepared from the hydrazo-compound by oxidation with ferric chloride or by the air in presence of water, crystallises in pale orange-yellow needles melting at  $187\text{--}188^\circ$ ; the *benzoyl* deriva-

tive, prepared by the Schotten-Baumann method, crystallises in orange-red needles melting at  $167-167.5^{\circ}$ ; the *phenylcarbamide* derivative forms orange-red prisms melting at  $129-130^{\circ}$ . When *p*-chlorophenylhydrazoacetaldoxime is oxidised with nitrous acid, *p*-chlorophenylazoxyacetaldoxime,  $C_6H_4Cl \cdot N_2O \cdot CMe \cdot NOH$ , is formed, crystallising in very pale yellow needles melting at  $101.5^{\circ}$ .

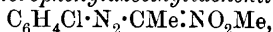
On boiling *p*-chlorophenylazoacetaldoxime with dilute sulphuric acid, hydrolysis takes place with the formation of acetaldoxime and *p*-chlorobenzenediazonium sulphate; from the former, acetic acid and hydroxylamine are produced, and from the latter *p*-chlorobenzeneazoimide, *p*-chlorophenol, *p*-chloroaniline, and nitrogen.

When *p*-chlorophenylazoacetaldoxime in acetic acid solution is treated with  $\alpha$ -naphthylamine and hydrochloric acid, *p*-chlorobenzenazo- $\alpha$ -naphthylamine,  $C_6H_4Cl \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$ , is formed; the latter was also prepared from a *p*-chlorobenzenediazonium salt and  $\alpha$ -naphthylamine, and crystallises in brown, lustrous needles melting at  $187.5-188^{\circ}$ ; the *hydrochloride* forms dark violet-red needles.

The synthesis of *p*-chlorophenylazoacetaldoxime was effected as follows. Nitroacetaldehyde *p*-chlorophenylhydrazone,



was prepared by adding a solution of *p*-chlorobenzenediazonium acetate to a solution of nitroethane in sodium hydroxide; it crystallises in orange-yellow, lustrous needles melting and decomposing at  $126-127^{\circ}$ . By the action of diazomethane, the last-mentioned substance is converted into *methyl p*-chlorophenylazoethylidenenitronate,

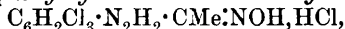


which crystallises in orange-red leaves with a bronze lustre and melts at  $112-112.5^{\circ}$ ; it is converted by boiling with water into *p*-chlorophenylazoacetaldoxime (m. p.  $187-188^{\circ}$ ) and formaldehyde. K. J. P. O.

**Action of Hydrogen Chloride on Arylazoacetaldoximes.** By EUGEN BAMBERGER and JOHANNES FREI (*Ber.*, 1902, 35, 82—91. Compare preceding abstracts).—2 : 4-Dichlorophenylhydrazoacetaldoxime *hydrochloride*,  $C_6H_3Cl_2 \cdot N_2H_2 \cdot CMe \cdot NOH, HCl$ , is formed when *p*-chlorophenylazoacetaldoxime (*loc. cit.*) is warmed with concentrated hydrochloric acid, and crystallises in needles melting at  $192-193^{\circ}$ ; the *base*, prepared from the hydrochloride by means of potassium acetate, forms white, lustrous needles melting and decomposing at  $138^{\circ}$ . On oxidation by air in presence of dilute sodium hydroxide, or by ferric chloride, 2 : 4-dichlorophenylazoacetaldoxime,  $C_6H_3Cl_2 \cdot N_2 \cdot CMe \cdot NOH$ , is obtained, crystallising in yellowish-red needles, melting and decomposing at  $207^{\circ}$ ; this substance was synthesised from nitroacetaldehyde-2 : 4-dichlorophenylhydrazone,  $C_6H_3Cl_2 \cdot N_2H \cdot CMe \cdot NO_2$ , which was prepared by the action of 2 : 4-dichlorobenzenediazonium acetate on nitromethane and crystallises in orange-yellow, silky needles melting at  $95.5^{\circ}$ ; with diazomethane, *methyl* 2 : 4-dichlorophenylazoethylidenenitronate,  $C_6H_3Cl_2 \cdot N_2 \cdot CMe \cdot NO_2Me$ , is formed as brick-red or ruby-red needles melting and decomposing at  $110-111^{\circ}$ . To convert the ester into the azoalldoxime and formaldehyde, it is best to boil it with a concentrated solution of calcium chloride, as the temperature of boiling water is not sufficiently high to bring about the change. On reduction

of the azoaldoxime, dissolved in acetone with zinc dust in the presence of ammonium chloride, the hydrazoacetaldoxime just described is formed.

2 : 4 : 6-Trichlorophenylhydrazoacetaldoxime hydrochloride,



formed by the action of dry hydrogen chloride on 2 : 4-dichlorophenylazoacetaldoxime dissolved in absolute ether, crystallises in white leaflets, and by treatment with a solution of potassium acetate is converted into the base, which crystallises in lustrous needles melting and decomposing at 156.5°. It is readily oxidised by ferric chloride to 2 : 4 : 6-trichlorophenylazoacetaldoxime,  $\text{C}_6\text{H}_2\text{Cl}_3 \cdot \text{N}_2 \cdot \text{CMe} \cdot \text{NOH}$ , which crystallises in brilliant, orange-red needles, melting and decomposing at 185—186°; this substance was also synthesised from nitroacetalddehyde 2 : 4 : 6-trichlorophenylhydrazone,  $\text{C}_6\text{H}_2\text{Cl}_3 \cdot \text{N}_2\text{H} \cdot \text{CMe} \cdot \text{NO}_2$ , which is prepared from 2 : 4 : 6-trichlorobenzene diazonium acetate and nitroethane, and crystallises in golden-yellow needles or leaflets melting at 98°; the sodium salt crystallises well. With diazomethane, it yields methyl 2 : 4 : 6-trichlorophenylazoethylidenenitronate,  $\text{C}_6\text{H}_2\text{Cl}_3 \cdot \text{N}_2 \cdot \text{CMe} \cdot \text{NO}_2\text{Me}$ , which crystallises in dark Bordeaux-red needles melting at 89—90°; on boiling with a concentrated solution of calcium chloride, it decomposes into formaldehyde and 2 : 4 : 6-trichlorophenylazoacetaldoxime. As already described (this vol., i, 246), the last-mentioned substance gives with hydrogen chloride the corresponding hydrazo-compound, acethydr-oxamic acid, and s-trichlorobenzene.

K. J. P. O.

**Supposed Isomerism of Diazothiosulphonates.** By B. DYBOWSKI and ARTHUR HANTZSCH (*Ber.*, 1902, 35, 268—271. Compare Troeger and Ewers, *Abstr.*, 1901, i, 171).—Diazothiosulphonates do not exist in two isomeric modifications, as stated by Troeger and Ewers (*loc. cit.*); the second amorphous form is in reality a mixture of the diazosulphone (azosulphone) and sulphur produced by the decomposition of the original diazothiosulphonate,  $\text{N}:\text{NAr} \cdot \text{S} \cdot \text{SO}_2\text{Ph} = \text{ArN}:\text{N} \cdot \text{SO}_2\text{Ph} + \text{S}$ .

*Naphthaleneazobenzene sulphone*,  $\text{C}_{10}\text{H}_7 \cdot \text{N}_2 \cdot \text{SO}_2\text{Ph}$ , separates from a mixture of ether and light petroleum as yellowish-brown crystals decomposing at 96°.

J. J. S.

**Azo-dyes from Phenylmethylglycine.** By JULIUS MAI [and, in part, with R. KAHN and WILHELM HEIMANN] (*Ber.*, 1902, 35, 576—582).—Phenylmethylglycine,  $\text{NMePh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , readily reacts with diazonium salts, yielding azo-dyes, which are characterised by their solubility and fastness to soap. Since a hydrochloric acid solution of the base readily decomposes, yielding carbon dioxide and dimethylaniline, it is necessary that the reaction shall be completed in the course of a very short time. The following compounds have been prepared :

*Benzeneazophenylmethylglycine*,  $\text{NPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , HCl, from benzenediazonium chloride.

The *p*-sulphonic acid,  $\text{SO}_3\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , brownish-violet, fluorescent crystals; it yields a sodium salt which is remarkably hygroscopic. The corresponding *m*-compound forms brown-coloured crystals and its hydrochloride is decomposed by water. The *p*-carboxylic acid,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , forms reddish-brown crystals.

*Diphenylazophenylmethylglycine*,  $\text{C}_6\text{H}_4\text{Ph} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ ,

from phenylmethylglycine and tetrazodiphenyl chloride, forms a dark brown precipitate.

Similar compounds with phenylglycine (Hausdörfer, Abstr., 1889, 1013) itself have been prepared.

*Benzeneazophenylglycine*,  $\text{NPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , golden, glistering crystals melting at  $140^\circ$  and insoluble in water. Its *p*-sulphonic acid,  $\text{SO}_3\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , decomposes above  $250^\circ$ ; the normal and acid sodium salts, the barium salt and hydrochloride were analysed.

*Methyl Benzeneazophenylcarbamate*,  $\text{NPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO}_2\text{Me}$ , forms yellowish-red needles. J. J. S.

**Discrimination between Basic and Acidic Functions in Proteid Solutions.** By HUGO SCHIFF (*Annalen*, 1902, 319, 287—303. Compare this vol., i, 85).—The amino-groups in egg-albumin, involved in the production of the biuret coloration, are destroyed by the action of nitrous acid, and are probably contained in complexes, such as  $\text{R} \cdot \text{CO} \cdot \text{NH}_2$ . Formaldehyde, on the other hand, reacting with proteids, biuret, and malonamide, gives rise to more soluble products which still furnish the biuret coloration; the nitrogen combining with the methylene group is, in all probability, present in residues of the type  $\text{R} \cdot \text{C}(\text{NH}_2) \cdot \text{CO}_2\text{H}$ . This hypothesis is supported by the fact that the proteids resemble the amino-carboxy-acids in becoming more acidic when their solutions are treated with formaldehyde, this reagent apparently severing the connection between the aminogen and carboxyl radicles, and allowing the acid functions of the latter to become manifest.

A solution of egg-albumin neutralised by *N*/10 potassium hydroxide solution in the presence of phenolphthalein is rendered acid by formaldehyde, and the amount of alkali required to restore neutrality indicates a molecular weight of 3281 for the proteid. Fish-gelatin behaves similarly, and its molecular weight is deduced to be 4680; in this case, the end point is clearly indicated by litmus as well as by phenolphthalein. The amount of decomposition which the proteid molecule undergoes on hydrolysis can be ascertained by this reaction. The quantity of alkali required to neutralise the acidity produced by formaldehyde in a solution of fish gelatin after boiling for several hours with potassium hydroxide solution is 45 times as great as in the case of the undecomposed proteid.

The following salts of aminoamides give the biuret reaction and develop a yellow coloration with a nickel salt in the presence of potassium hydroxide. *a* *Aminopropionamide hydrobromide*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{CHMe} \cdot \text{NH}_2 \cdot \text{HBr}$ , forms a syrupy mass which slowly crystallises. *a* *Aminoisobutyramide hydrobromide*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{CMe}_2 \cdot \text{NH}_2 \cdot \text{HBr}$ , separates from dilute methyl alcohol in crystals, stable in the atmosphere, which melt and decompose at  $210$ — $220^\circ$ . *a* *Amino-isovaleramide hydrobromide*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{CHPr}^s \cdot \text{NH}_2 \cdot \text{HBr}$ , is a crystalline substance decomposing at  $200^\circ$  (compare Schiff, Abstr., 1896, i, 284, 632). G. T. M.

**Estimation of Sulphur in Proteids.** By THOMAS B. OSBORNE (*Zeit. anal. Chem.*, 1902, 41, 25—35; from *Studies Research Lab. Connecticut Exper. Stat.*, 1900, 443—471).—The total sulphur was

estimated by fusing the proteid with sodium peroxide and weighing as bariumsulphate. The loosely combined sulphur was estimated by Schulz's method (Abstr., 1898, i, 502), which consists in cohobating the substance with sodium hydroxide, lead acetate, and metallic zinc (to prevent oxidation) for several hours, and ascertaining the amount of sulphur converted into lead sulphide. In another method, the zinc was omitted and the mixture was heated in an autoclave at 135—165° in an atmosphere free from oxygen. Except vicilin, phaseolin, and conglutin, all the proteids examined showed a constant percentage of total sulphur, and, omitting phaseolin and casein, they contain from  $\frac{1}{3}$  to  $\frac{2}{3}$  of their sulphur in the loosely combined condition. The author has previously given reasons for assuming that the molecular weights of the proteids approximate to 15,000 (*J. Amer. Chem. Soc.*, 1899, 21, 486). If, for such of the proteids as can be obtained in crystals, and the constancy of composition of which is a criterion of purity, the simplest empirical formula be multiplied by the number which will give a molecular weight nearest to 15,000, the total sulphur will be found to range from 2 to 11 atoms. In those proteids which contain only 2 atoms of sulphur, almost exactly one-half of it is loosely combined. Proteids with a larger number of sulphur atoms in the molecule yield less than half their total sulphur when digested with sodium hydroxide. Mörner and Embden have found cystin and cystein in a variety of proteids, and Mörner has discovered another sulphuretted complex which yields lead sulphide on digestion with alkaline lead solution. It is well known that only half the sulphur of cystin and cystein can be removed as lead sulphide by Schulz's method. The suggestion is therefore made that cystin or cystein is a constituent of only those proteids which are comparatively rich in sulphur.

Casein forms a marked exception; of the 0.8 per cent. of total sulphur, only 0.1 can be obtained as lead sulphide. M. J. S.

**Estimation of Iodic and Hydriodic Acids formed in the Iodination of Proteids.** By C. H. L. SCHMIDT (*Zeit. physiol. Chem.*, 1901, 34, 194—206. Compare following abstract).—The amounts of iodic and hydriodic acid, produced when proteids are warmed with water and iodine for definite periods of time have been estimated and the results expressed in the form of curves. The proteids investigated were vitellin, crystallised egg-albumin, and "Casein Hammarsten." The whole process appears to be termolecular. J. J. S.

**Formation of Iodic Acid in the Iodination of Crystallised Egg-albumin.** By C. H. L. SCHMIDT (*Zeit. physiol. Chem.*, 1901, 34, 55—65).—When a solution of crystallised egg-albumin is boiled for a short time with iodine, oxidation accompanied by the formation of hydrogen iodide occurs, and at the same time amino-groups are eliminated from the molecule in the form of ammonium iodate and iodide. Free hydriodic acid can only exist in the presence of an iodide and iodate within certain limits; if these are exceeded, reduction of the iodate begins. This accounts for the fact that the amount of iodate present in the iodinated proteid solution never exceeds a certain small maximum. The formation of iodate by the action of iodine on concentrated proteid solutions at the

ordinary temperature is a characteristic of basic proteids. Carbamide, arginine, and guanidine- $\alpha$ -aminovaleric acid yield iodic acid. Aspartic acid does not. J. J. S.

**Oxidation of Nitrogenous Substances.** By W. FALTA (*Ber.*, 1902, **35**, 294—296).—A reply to Jolles (this vol., i, 86. Compare Abstr., 1901, ii, 705). W. A. D.

**Proteid-dissolving Enzyme in Malt.** By E. EHRICH (*Bied. Centr.*, 1901, **30**, 857; from *Der Bierbrauer*, 1901, 4).—Malt is shown to contain an enzyme which dissolves proteids. The enzyme is very active in many malts, less active in others. N. H. J. M.

**Emulsin.** By G. HEUT (*Arch. Pharm.*, 1901, **239**, 581—589).—The hydrolysing action of certain lichens on amygdalin and other glucosides was studied by Bourquelot's method (Abstr., 1894, ii, 63) and Hérissé (*Recherches sur l'émulsine, Lons-le-Saunier*, 1899). *Polyporus Clusianus*, *Cladonia delicata* and *C. digitata*, *Imbricaria saxatilis* and *Parmelia tenella* exerted this action on amygdalin; *Xanthoria parietina* did not; *Peltigera horizontalis* did if it had grown on a tree, not when it had grown on the ground. *Parmelia obscura* hydrolysed amygdalin readily when it had grown on a fence; the variety *virella*, which had grown on an Italian poplar, had but little action.

Hérissé was unable to ascertain whether pepsin digested emulsin in the presence of dilute hydrochloric acid or not, because in a blank experiment without pepsin the acid alone deprived the emulsin of its power to liberate glucose from amygdalin. The author finds that  $\frac{1}{2}$ —1 per cent. malic acid certainly weakens, but does not destroy, the hydrolysing action of emulsin on amygdalin, but that if 1 per cent. of pepsin is added no sugar is formed. Evidently the pepsin does digest and destroy the emulsin. C. F. B.

**Superoxydases.** By ROBERT W. RAUDNITZ (*Zeit. Biol.*, 1901, **42**, 91—106).—Fresh milk decomposes hydrogen peroxide with the formation of free oxygen; this catalytic action is lost when the milk is boiled, and is attributed to a ferment termed a peroxydase. Thiocyanates have an inhibitory influence on this action, and this is due to the production of hydrocyanic acid. The decomposition of hydrogen peroxide by blood is mainly due to hæmoglobin. When this substance is recrystallised many times, it has the same catalytic property, this is also possessed by methæmoglobin and hæmatin, but not by hæmatoporphyrin; the property is therefore probably due to the constituent of hæmoglobin which contains iron. W. D. H.

**Action of Trypsin on Gelatin.** By FRIEDRICH REICH-HERZBERGE (*Zeit. physiol. Chem.*, 1901, **34**, 119—121).—Kühne stated that gelatin under the influence of trypsin yields neither leucine nor glycine. Certainly tryptic digestion does not lead to any profound decomposition of gelatin, but there is always a small yield of leucine. W. D. H.

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## Organic Chemistry.

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**Linking of Carbon Atoms in the Paraffin Series.** By SIMA M. LOSANITSCH (*Bull. Soc. Sci. Bucuresci-România*, 1901, 353—396).—The author develops a method for calculating the number of possible isomerides of the paraffins, and gives the numbers in a table for the isomerides from  $\text{CH}_4$  to  $\text{C}_{16}\text{H}_{34}$ .

A nomenclature is also suggested so as to indicate the number of carbon atoms, the nature, number, and sequence of the side-chains, and the position of the side-chains. J. McC.

**Action of Potassium Hydride on Ethyl Iodide and Methyl Chloride. Formation of Ethane and Methane.** By HENRI MOISSAN (*Compt. rend.*, 1902, 134, 389—392).—When ethyl iodide is heated with potassium hydride in sealed tubes at 180—200°, ethane is formed, together with potassium iodide. Methyl chloride and potassium hydride under the same conditions yield methane. A small quantity of hydrogen is liberated in both cases, but there is no liberation of carbon or iodine or chlorine. C. H. B.

**Decomposition of Acetylene during its Combustion.** By FERNAND GAUD (*Compt. rend.*, 1902, 134, 175—177).—The incrustation of carbon which forms round the orifices of acetylene burners is due to the decomposition of polymerides of this hydrocarbon. Since the polymerisation takes place only at temperatures above 100°, it follows that this change is due to the preliminary heating of the gas in the burner. An ordinary Manchester acetylene burner, when supplied with pure acetylene under a pressure sufficient to give a full flame, is only slightly coated with carbon after 12—13 hours, and maintains its efficiency even after 100 hours' use. When, however, the flame is turned down, the slow stream of gas becomes considerably heated in passing through the burner, polymerisation occurs, and a rapid incrustation is produced. G. T. M.

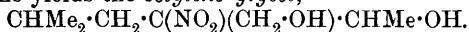
**Study of the Acetylene Hydrocarbons: Synthesis of Acetylenoid Ketones and their Hydrolysis by Alkali Hydroxides. New Method of Synthesising  $\beta$ -Diketones.** By CHARLES MOUREU and RAYMOND DELANGE (*Ann. Chim. Phys.*, 1902, [vii], 25, 239—268).—A *résumé* of work already published (compare Abstr., 1900, i, 397; 1901, i, 14, 352, 359, 581, and this vol., i, 164). G. T. M.

**Presence of *n*-Butyl Alcohol in Fusel Oil from Grain.** By OSKAR EMMERLING (*Ber.*, 1902, 35, 694—695).—Ten litres of the fusel oil from grain yielded, on fractionation, 15 grams of a product boiling at 114—118°; this substance was impure *n*-butyl alcohol, which was purified by successive conversion into iodide and acetate, 2.5 grams of the pure alcohol being ultimately obtained. This compound is most

conveniently prepared from glycerol by fermentation with cow-dung; the fermenting agent when dried preserves its power for many years.

G. T. M.

**Some Derivatives of Primary Nitroisopentane.** By THÉOPHILE MOUSSET (*Bull. Acad. roy. Belg.*, 1901, 622—656).—The author has studied the condensation of primary nitroisopentane with aldehydes; the action on it of sodium and halogens, of piperidylmethyl alcohol, and of reducing agents. The compound can condense either with 1 or with 2 mols. of aldehyde. With 1 mol. of formaldehyde it yields the *β*-nitroisohexyl alcohol,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{NO}_2)\cdot\text{CH}_2\cdot\text{CHMe}_2$ , a colourless liquid with a disagreeable odour and bitter taste, which boils at  $141^\circ$  under 32 mm. pressure, has a sp. gr. 1.060 at  $13^\circ$ , and is insoluble in water, but soluble in ether or alcohol. It forms a sodium salt, and on reduction with aluminium amalgam yields the corresponding *aminoisohexyl alcohol*, a colourless liquid which boils at  $198\text{--}200^\circ$  under 768 mm. pressure, has a sp. gr. 0.9173 at  $13^\circ$ , and yields a crystalline *platinichloride*. The amine forms a crystalline *dibenzoyl* derivative which melts at  $124\text{--}125^\circ$ ; with ethyl oxalate, it yields the compound  $\text{C}_2\text{O}_2[\text{NH}\cdot\text{CH}(\text{CH}_2\cdot\text{OH})\cdot\text{CH}_2\cdot\text{CHMe}_2]_2$ , which crystallises in pure white needles melting at  $99\text{--}100^\circ$ , and with picrolonic acid it forms a yellow salt which decomposes at about  $245\text{--}247^\circ$ . With phenylthiocarbimide, it gives a non-crystallisable substance. *α*-Chloro-*β*-nitroisohexane, formed by the action of phosphorus pentachloride on nitroisohexyl alcohol, is a very mobile, faintly greenish-coloured liquid, which boils at  $209\text{--}210^\circ$  under atmospheric pressure and has a sp. gr. 1.090 at  $18^\circ$ . The *nitroisohexyl acetate* is a yellowish liquid which boils at  $147^\circ$  under 40 mm. pressure, and has a sp. gr. 1.059 at  $13^\circ$ . *α*-Amino-*β*-isohexyl alcohol is a colourless liquid which boils at  $198\text{--}200^\circ$ , and has a sp. gr. 0.890 at  $17^\circ$ . It forms a crystalline *platinichloride*, a crystalline *dibenzoyl* derivative which melts at  $128^\circ$ , and also a crystallisable salt with picrolonic acid which decomposes at about  $240\text{--}243^\circ$ . With 2 mols. of formaldehyde, primary nitroisopentane yields a heptylene glycol,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{C}(\text{NO}_2)(\text{CH}_2\cdot\text{OH})_2$ , which crystallises in white needles and melts at  $98^\circ$ . With acetaldehyde, nitroisopentane forms nitro-*γ*-isoheptanol,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NO}_2)\cdot\text{CHMe}\cdot\text{OH}$ , a colourless liquid which boils at  $132^\circ$  under 30 mm. pressure and has a sp. gr. 1.020 at  $13^\circ$ . With a mixture of formaldehyde and acetaldehyde, nitroisopentane yields the *octylene glycol*,



By passing chlorine into an aqueous solution of the sodium derivative of nitroisopentane, *chloronitroisopentane*,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{NO}_2$ , is produced; it is a colourless, mobile liquid which boils at  $178^\circ$  under 750 mm. pressure, has a sp. gr. 1.177 at  $13^\circ$ , and is insoluble in water but soluble in alkalis, ether, or alcohol. *Bromonitroisopentane*, obtained in a similar manner, boils at  $119\text{--}120^\circ$  under 80 mm. pressure, and has a sp. gr. 1.453 at  $13^\circ$ . With formaldehyde, it yields *β*-bromo-*β*-nitroisohexyl alcohol,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CBr}(\text{NO}_2)\cdot\text{CH}_2\cdot\text{OH}$ , a brownish-coloured liquid which boils at  $159\text{--}161^\circ$  under 55 mm. pressure, and has a sp. gr. 1.461 at  $13^\circ$ .

With piperidylmethyl alcohol, nitroisopentane yields the compound



$\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{NO}_2)(\text{CH}_2 \cdot \text{C}_5\text{NH}_{10})_2$ , a white, crystalline substance which melts at  $40^\circ$ .

The author has also succeeded in obtaining methylisobutylamine by the direct reduction of primary nitroisopentane with tin and hydrochloric acid.

A. F.

**A Glycol Isomeric with Pinacone.** By ADOLF FRANKE (*Monatsh.*, 1901, 22, 1067—1072).—Diacetone alcohol (see Abstr., 1900, ii, 395) is reduced by aluminium amalgam to  $\beta$ -methylpentane- $\beta\delta$ -diol,  $\text{OH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{OH}$ , which boils at  $190$ — $194^\circ$  under 740 mm. pressure, does not solidify at  $-20^\circ$ , and has a sp. gr. 0.9231 at  $22^\circ$ . The mol. weight was found in two determinations to be 117.7 and 119.5. The *diacetate* distils at  $95^\circ$  under 12 mm. pressure. When boiled with dilute sulphuric acid, the glycol does not yield pinacoline. This new  $\beta$ -glycol is isomeric with pinacone, which must therefore be an  $\alpha$ -glycol.

G. Y.

**Hydroxyisopropylhypophosphorous Acid.** By CH. MARIE (*Compt. rend.*, 1902, 134, 286—288. Compare Abstr., 1901, i, 635).—Hydroxyisopropylhypophosphorous acid ( $\text{H}_3\text{PO}_2, \text{C}_3\text{H}_6\text{O}$ ) is best purified by fusing it under dry ether and then decanting the liquid; it forms a lustrous, radiating, solid mass which melts at  $45^\circ$  (compare *loc. cit.*). At  $110$ — $120^\circ$ , or when boiled with acids, it decomposes into hypophosphorous acid and acetone; it is readily oxidised by mercuric chloride or ferric salts to the acid  $\text{H}_3\text{PO}_3, \text{C}_3\text{H}_6\text{O}$ , and when boiled with acetone yields the acid  $\text{H}_3\text{PO}_2, 2\text{C}_3\text{H}_6\text{O}$ . The *cobalt* salt crystallises in rose-coloured, silky tufts with  $4\text{H}_2\text{O}$ , and is blue when anhydrous; the *nickel* salt crystallises with  $4\text{H}_2\text{O}$ , and is green, or pale yellow when anhydrous; the *copper* salt is pale blue, and crystallises with  $\text{H}_2\text{O}$ ; when heated in carbon dioxide at  $100^\circ$ , it decomposes into copper, and hydroxyisopropylphosphorous, and hydroxyisopropylhypophosphorous acids. It is similarly decomposed by boiling water, but in the presence of air, copper hydroxyisopropylphosphite is formed. The *silver* salt is anhydrous, and in solution soon darkens and deposits silver. The *methyl* and *ethyl* esters obtained from the silver salt are viscous liquids; the former has a sp. gr. 1.212 and  $n_D$  1.462 at  $16^\circ$ .

K. J. P. O.

**Glycero-arsenic Acid.** By VICTOR AUGER (*Compt. rend.*, 1902, 134, 238—240).—When arsenic acid and glycerol are heated together, glycero-arsenic acids are formed, with elimination of one or two mol. proportions of water as the case may be. If calcium dihydrogen arsenate is heated with glycerol, a calcium glycero-arsenate is obtained as a white, deliquescent solid. Both the acids and the calcium salt are, however, at once decomposed by water, and hence cannot be formed in solution (compare Pagel, Abstr., 1901, i, 498).

C. H. B.

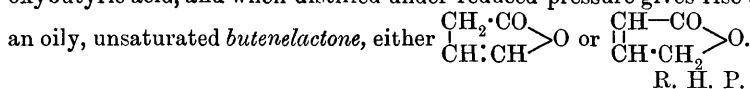
**New Synthesis of Formic Acid.** By HENRI MOISSAN (*Compt. rend.*, 1902, 134, 261—264. Compare this vol., ii, 136).—A rapid stream of pure dry carbon dioxide is passed over crystalline potassium hydride which has been volatilised along a glass tube. The potassium hydride quickly changes in appearance, and much heat is developed.

To avoid a deposition of carbon, which takes place if the temperature rises to any extent, the tube must be cooled. The substance formed from potassium hydride and carbon dioxide proved to be potassium formate.

Carbon monoxide and potassium hydride react but slowly, even at 210°. If a mixture of hydrogen (1 vol.) and carbon monoxide (2 vols.) is heated in contact with potassium, a fairly rapid absorption of the gases by the metal takes place; at the end of the reaction, the metal has become replaced by a mixture of carbon and crystalline needles, which are potassium formate.

K. J. P. O.

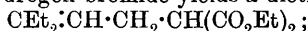
**Vinylacetic Acid.** By FRITZ FICHTER and FERDINAND SONNEBORN (*Ber.*, 1902, 35, 938—943).—The impure vinylacetic acid previously obtained (*Abstr.*, 1899, i, 255) can be purified from *isocrotonic* acid, since sodium vinylacetate is much less soluble in alcohol than sodium crotonate. The pure acid boils at 163°, or at 71° under 12—14 mm. pressure, has a sp. gr. 1.013 at 15°/15°,  $n_D$  1.42572 at 15°, and a conductivity  $K=0.0051$ . The *calcium* salt crystallises, with  $H_2O$ , in yellow, lustrous needles, the *barium* salt in small, lustrous, felted needles, and the *sodium* salt in lustrous laminæ. When treated with mineral acids, vinylacetic acid yields crotonic acid. The formula of the acid is proved to be  $CH_2:CH \cdot CH_2 \cdot CO_2H$ , as the substance, when treated with bromine in carbon bisulphide solution, forms  $\beta$ -dibromobutyric acid, which is a crystalline compound melting at 49—50°, and when treated with water yields  $\beta$ -hydroxybutyrolactone.  $\beta$ -Hydroxybutyrolactone, when treated with baryta water, yields the barium salt of  $\beta$ -dihydroxybutyric acid, and when distilled under reduced pressure gives rise to an oily, unsaturated *butenelactone*, either



R. H. P.

**Preparation of  $\gamma\delta$ -Unsaturated Monobasic Acids.** By A. A. SOLONINA (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 734—739).—The author has further studied the methylhexenoic acid of the composition  $CMe_2:CH \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , already prepared by Barbier (*Bull. Soc. Chim.*, 1887, [ii], 47, 701) and by Léser (*Abstr.*, 1899, i, 414), which he has obtained by the action of ethyl sodiomalonate on the additive compound of hydrogen bromide and isoprene. The acid has the sp. gr. 0.9864 at 0°/0° and  $n_D$  1.45041 at 17°; the molecular refraction (Lorenz and Lorentz formula) is 34.91, the number calculated from the formula being 35.93. The *silver*, *calcium* (+ 2 $H_2O$ ), *barium* (+ 3 $H_2O$ ), and *lead* (+ 6 $H_2O$ ) salts were prepared as well as the methyl and ethyl esters. The last-named compound forms, with nitrosyl chloride, a *substance* melting at 75° and having the probable constitution  $CMe_2Cl \cdot C(NO)H \cdot CH_2 \cdot CH_2 \cdot CO_2Et$ .

The action of ethyl sodiomalonate on the additive compound of diethylallene with hydrogen bromide yields a diethyl ester,



on heating the corresponding acid, it evolves carbon dioxide and acetic acid, the residue consisting of an *acid*,  $CEt_2:CH \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , which boils at 232—236° and has the sp. gr. 0.9589 at 0°/0° and 0.9459

at 15°/0°. It decolorises 1 per cent. potassium permanganate solution and becomes viscous when cooled in a mixture of ether and solid carbon dioxide. Its *silver* salt, which is white and amorphous, is sparingly soluble in water and readily decolorises permanganate solution.

T. H. P.

**Solid Acids of Olive Oil.** By D. HOLDE (*Chem. Centr.*, 1902, i, 177—178; from *Mitt. Techn. Vers.-A. Berlin*, 19, 115—117. Compare Abstr., 1901, i, 577).—The results of an examination of the solid acids of olive oil by fractional precipitation with magnesium acetate by Heintz's method, together with determinations of the melting points and mol. weights of the separate fractions and comparison with two artificial mixtures of stearic acid (1 mol.), melting at 69°, and palmitic acid (1 mol.) melting at 62.1°, show that the acids obtained from the oil do not consist of stearic and palmitic acids in these proportions. The mol. weights of the various fractions were all found to correspond with the formula  $C_{17}H_{34}O_2$ . The acids are therefore derived from a glyceride of the formula  $C_3H_5(C_{17}H_{33}O_2)_2 \cdot C_{18}H_{33}O_2$ , and not from oleopalmitostearin.

E. W. W.

**Formation of Lactic Acid from Pentoses by the Action of Potassium Hydroxide.** By K. KATSUYAMA (*Ber.*, 1902, 35, 669—671).—The statement of Araki (*Zeit. physiol. Chem.*, 19, 463) that arabinose yields lactic acid when heated with sodium hydroxide is confirmed, and it is shown that xylose also yields lactic acid when heated with potassium hydroxide.

T. M. L.

**Trimethylpentanolic Acid.** By KARL MICHEL and KARL SPITZAUER (*Monatsh.*, 1901, 22, 1109—1118).— $\alpha\gamma$ -Trimethyl- $\beta$ -pentanolic acid,  $CHMe_2 \cdot CH(OH) \cdot CMe_2 \cdot CO_2H$ , is best obtained by preparing the ethyl ester by the condensation of isobutaldehyde and ethyl bromoisobutyrate by the action of zinc (Reformatsky's method). On hydrolysis of the ester by potassium hydroxide, part of the acid decomposes to isobutyric acid and isobutaldehyde; the latter, in presence of potassium hydroxide, undergoes the normal condensation to octylene-glycol and trimethylpentanolic acid. As the acid decomposes most easily at the moment of formation, the reaction proceeds until the whole of the isobutaldehyde is converted into octoglycol and isobutyric acid (see Lieben, Abstr., 1901, i, 449).

G. Y.

**Action of Alkyl Halogen-substituted Propionates on Sodio-acetylacetone.** By FR. MARCH (*Compt. rend.*, 1902, 134, 179—181. Compare Abstr., 1901, i, 312, 596).—Ethyl  $\beta\beta$ -diacetyl- $\alpha$ -methylpropionate,  $CHAc_2 \cdot CHMe \cdot CO_2Et$ , obtained by the interaction of ethyl  $\alpha$ -bromopropionate on sodioacetylacetone at 120—140°, boils at 149—151° and at 128—130° under pressures of 33 and 10 mm. respectively, and has a sp. gr. 1.067 at 15°; it is insoluble in water but dissolves in ether or alcohol, develops a deep red coloration with ferric chloride, and is decomposed by aqueous and alcoholic sodium hydroxide solutions into sodium lævulate and ethyl lævulate respectively, sodium acetate being a product common to both hydrolyses.

When treated with hydroxylamine hydrochloride and potassium carbonate, the ester yields its *dioxime*,  $C_{10}H_{18}O_4N_2$ , melting at  $133^\circ$ ; this compound is accompanied by *ethyl dimethyloxazole- $\alpha$ -propionate*,  $N:CM_e \begin{smallmatrix} O \\ O \end{smallmatrix} \cdot CM_e \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} C \cdot CHMe \cdot CO_2Et$ , an oil boiling at  $143\text{--}145^\circ$  under 21 mm. pressure. The corresponding acid,  $C_8H_{11}O_3N$ , crystallises in colourless needles and melts at  $106^\circ$ ; it is soluble in ether or water; its green *copper* salt melts at  $254\text{--}255^\circ$ .

If, in preparing the dioxime, the boiling is continued for 24 hours, this substance undergoes condensation with elimination of alcohol, giving rise to the compound  $O \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} CO \cdot CHMe \\ N = CM_e \end{smallmatrix} \begin{smallmatrix} \diagdown \\ \diagup \end{smallmatrix} CH \cdot CM_e \cdot NOH$ ,

which melts at  $203\text{--}204^\circ$  and develops a deep red coloration with alcoholic ferric chloride. Semicarbazide reacts with ethyl  $\beta\beta$ -diacetyl- $\alpha$ -methylpropionate to form the compound  $C_{12}H_{22}O_4N_6 \cdot \frac{1}{2}H_2O$ ; this product, which is sparingly soluble in the ordinary solvents, when crystallised from ethyl acetate, melts at  $207\text{--}208^\circ$ , and then has the composition  $C_{12}H_{22}O_4N_6 \cdot \frac{1}{2}CH_3 \cdot CO_2Et$ .

*Ethyl  $\gamma\gamma$ -diacetylbutyrate*,  $CHAc_2 \cdot CH_2 \cdot CH_2 \cdot CO_2Et$ , produced by the interaction of ethyl  $\beta$ -chloropropionate and sodioacetylacetone, boils at  $154\text{--}155^\circ$  under 15 mm. pressure, and develops a red coloration with ferric chloride; its *copper* derivative,  $Cu_2(C_{10}H_{15}O_4)_2$ , melts at  $209^\circ$ .  
G. T. M.

**Action of Aluminium Chloride on certain Anhydrides in Chloroform Solution.** By MARCEL DESFONTAINES (*Compt. rend.*, 1902, 134, 293—296).—Following the observations of Tiemann (*Abstr.*, 1897, i, 199) on the action of sulphuric acid on camphoric acid, when carbon monoxide is eliminated and a  $\gamma$ -lactone, terpenylic acid, formed, and the experiments of Blanc (*Bull. Soc. Chim.*, 1901, [iii], 25, 68) on the formation of *isolaunonic* acid by the action of aluminium chloride on camphoric anhydride, the action of the latter reagent has been tried on the anhydrides of dicarboxylic acids, in which one of the carboxyl groups is tertiary.

$\alpha\alpha$ -Dimethylglutaric anhydride, dissolved in chloroform, reacts vigorously with aluminium chloride; carbon monoxide is evolved and *isohexolactone*,  $\begin{smallmatrix} CH_2 - CO \\ | \\ CH_2 \cdot CM_e \end{smallmatrix} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} O$ , formed; the identity of the latter was established by conversion into ethyl  $\gamma$ -bromoisohexoate. At the same time,  $\alpha\alpha$ -dimethylglutaric and pyroterebic acids are produced.

Dimethylsuccinic anhydride and aluminium chloride yield carbon monoxide and dimethylacrylic acid, dimethylsuccinic acid being formed at the same time.  
K. J. P. O.

**Action of Ethyltrioxymethylene Chloride on Ethyl Sodiomalonate.** By G. H. COOPS (*Rec. Trav. Chim.*, 1901, 20, 430—434).—By the action of hydrogen chloride on formaldehyde, ethyltrioxymethylene chloride,  $OEt \cdot CH_2 \cdot O \cdot CH_2 \cdot O \cdot CH_2Cl$ , is formed, among other substances. On adding this mixture to ethyl sodiomalonate, a product is obtained which, on hydrolysis with potassium hydroxide,

yields  $\beta$ -isomalic acid,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})_2$ , of which the lead and calcium salts were prepared. K. J. P. O.

**A Chlorogalactonic (Chlorotetrahydroxyhexoic) Acid.** By OTTO RUFF and ARTHUR FRANZ (*Ber.*, 1902, 35, 943—948).—When galactonolactone is treated with acetyl chloride, a *monochlorotriacetyl* derivative,  $\text{C}_{12}\text{H}_{15}\text{O}_8\text{Cl}$ , is obtained; this crystallises in rhombic prisms, which sinter at  $95\text{--}96^\circ$  and melt at  $98^\circ$  (corr.), and has  $[\alpha]_D -22\cdot41^\circ$  at  $20^\circ$ . When treated with alcoholic ammonia, it yields the *amide* of chlorogalactonic acid  $\text{C}_6\text{H}_{12}\text{O}_5\text{NCl}$ , which crystallises in silky needles melting at  $194\cdot5^\circ$  (corr.) and has  $[\alpha]_D +71\cdot43^\circ$  at  $20^\circ$ . The action of liquid ammonia yields insoluble substances of undetermined composition decomposing at  $227^\circ$  and  $240\text{--}250^\circ$  respectively. The *anilide* of chlorotriacetyl galactonic acid,  $\text{C}_{12}\text{H}_{15}\text{O}_8\text{Cl}\cdot\text{NH}_2\cdot\text{Ph}$ , crystallises in silky needles, which melt and decompose at  $187\cdot5^\circ$ . The *piperidide* of chlorogalactonic acid,  $\text{C}_{11}\text{H}_{20}\text{O}_5\text{NCl}$ , is deliquescent and crystallises with 1 mol. of piperidine in colourless prisms. The authors find the specific rotation of galactonolactone to be  $[\alpha]_D -77\cdot61^\circ$  at  $20^\circ$ , altering in three days to  $-67\cdot89^\circ$ ; the melting point is  $134\text{--}136^\circ$  (corr.) (compare Tollens and Schnelle, *Abstr.*, 1892, 1432).

R. H. P.

**Influence of Ammonium Paramolybdate on the Specific Rotatory Power of Sodium Hydrogen Tartrate.** By HERMANN IRZIG (*Ber.*, 1902, 35, 690—692. Compare Rosenheim and Itzig, *Abstr.*, 1900, i, 272; Klason and Köhler, this vol., i, 75).—A maximum specific rotatory power is reached in solutions of sodium hydrogen tartrate when ammonium paramolybdate is added in the ratio of 0.692 of molybdate to 0.576 of tartrate. T. M. L.

**Compound of Tartaric Acid with Formaldehyde.** By WILHELM STERNBERG (*Chem. Centr.*, 1902, i, 299; from *Pharm. Zeit.*, 1901, 46, 1003—1004. Compare *Abstr.*, 1901, i, 120).—*Diformal tartrate* or

*dimethylene tartrate*,  $\begin{array}{c} \text{O}-\text{CO} \\ | \\ \text{CH}_2-\text{O} \end{array} > \text{CH}\cdot\text{CH} < \begin{array}{c} \text{CO}\cdot\text{O} \\ | \\ \text{O}-\text{CH}_2 \end{array}$ , prepared by dissolving trioxymethylene in molten tartaric acid and adding sulphuric acid to the viscous syrup which is formed, crystallises in colourless needles, melts at  $120^\circ$ , boils at  $296^\circ$ , and may be sublimed; it is easily soluble in alcohol, acetone, ethyl acetate, or chloroform, is decomposed by dilute sodium carbonate solution even at a blood heat, and more quickly by alkali hydroxides, but is not so readily attacked by acids. This compound is not the methyl ester of methylenetartaric acid, since repeated evaporation of its aqueous solution is sufficient to decompose it with liberation of tartaric acid; the behaviour of malonic and succinic acids with formaldehyde also justifies this conclusion.

Attempts to prepare methylenetartaric acid by digesting tartaric acid with formalin and hydrochloric acid failed. E. W. W.

**Action of Formaldehyde on Citric Acid.** By WILHELM STERNBERG (*Chem. Centr.*, 1902, i, 299—300; from *Pharm. Zeit.*, 1901, 46, 1004. Compare *Abstr.*, 1901, i, 120, and 1902, i, 76).—*Methylene-*

*citric acid*,  $C_7H_8O_7$ , prepared by heating citric acid with paraformaldehyde at  $140-160^\circ$ , or by evaporating formalin and hydrochloric acid with citric acid, crystallises from water in prisms grouped together in star-like aggregates, melts and decomposes at  $205^\circ$ , is readily soluble in hot, but only slightly in cold, water, is not decomposed by boiling with water or dilute acids, but is attacked by alkali hydroxides or carbonates. The silver salt is a white, amorphous powder, and is soluble in 1500 parts of water.

E. W. W.

**Characterisation of Pseudo-acids by Conductivity Determinations of Aqueous-Alcoholic Solutions.** By ARTHUR HANTZSCH and E. VOEGELEN (*Ber.*, 1902, 35, 1001—1009).—This is an additional method for the characterisation of pseudo-acids, and depends on the different course of dissociation of true and pseudo-acids in aqueous-alcoholic solution.

The compound, which is thought to be a pseudo acid, is dissolved in alcohol of different strengths, usually containing 25, 40, 50, 75, and 100 per cent. of alcohol by volume. The electrical conductivities of these solutions are measured, and the numbers compared with numbers obtained from solutions of the same strength, but containing a true acid, the dissociation constant of which, in pure water, is practically the same as that of the supposed pseudo-acid. If the conductivity numbers for the solutions of the true acid decrease much more rapidly than the numbers for the solutions of the pseudo-acid as the strength of the alcohol is increased, then the compound must be a pseudo-acid. The following examples illustrate the relationship of the numbers obtained for a true and pseudo-acid. Violuric acid (pseudo-acid),  $K=0.0027$ . Lævulic acid (true acid),  $K=0.0024$ :

Per cent. alcohol ...	0	25	40	50	75	100
Violuric acid $\mu_{64}$ ...	14.5	6.53	4.13	2.91	0.90	0.23
Lævulic acid $\mu_{64}$ ...	13.85	4.65	2.35	1.49	0.32	—
Nitroacetone $\mu_{128}$ ...	12.40	6.36	—	2.74	0.74	—
Acetic acid $\mu_{128}$ ...	16.99	6.12	—	1.93	—	—

Numerous other examples are given.

It does not necessarily follow because the numbers for the supposed pseudo-acid solutions decrease as rapidly as, or more rapidly than, those of a similar true acid, that the compound is not a pseudo-acid, for example, nitroacetophenone and succinic acid:

Alcohol per cent. ....	0	25	50	75
Nitroacetophenone $\mu_{256}$ ..	41.1	10.0	4.0	1.2
Succinic acid $\mu_{256}$ .....	43.9	15.8	5.3	1.4

J. J. S.

**Paraldol and Viscid Acetalddol.** By ALEXANDER KARL NOWAK (*Monatsh.*, 1901, 22, 1140—1145).—Molecular weight determinations by freezing point and boiling point methods show that paraldol and the viscid acetalddol have the same molecular weight, which in dilute solutions approaches the unimolecular, in concentrated solutions the bimolecular, value.

Paraldol sublimes unchanged at 73° under 1—2 mm. pressure. The viscid aldol distils at 73° under 16 mm. pressure and condenses partly as the crystalline paraldol and to a small extent as the mobile aldol.

G. Y.

**Alkoxides of Bromal.** By EMILIO GABUTTI (*L'Orosi*, 1901, 24 364—366).—*Bromal glycolate*,  $C_2H_4[O\cdot CH(OH)\cdot CBr_3]_2$ , prepared by the action of bromal (2 mols.) on ethylene glycol (1 mol.), is a dense, colourless oil having a pungent odour; it boils at 145—150° and is soluble in alcohol or ether.

*Bromalglycol monoacetate*,  $CBr_3\cdot CH(OH)\cdot O\cdot CH_2\cdot CH_2\cdot OAc$ , obtained from bromal and ethylene glycol monoacetate, is a colourless oil of pungent odour, which boils at 168—169° and dissolves in ether or alcohol.

T. H. P.

**Formation of Aldehydes and Ketones from Haloid Derivatives of Ethylene Hydrocarbons.** By K. KRASSUSKY (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 791—808).—When  $\beta\gamma$ -dimethyl- $\beta$ -butylene is mixed with water and lead oxide and the liquid shaken from time to time, pinacone,  $OH\cdot CMe_2\cdot CMe_2\cdot OH$ , is formed to the extent of 57 per cent. of the theoretical yield, together with a smaller quantity of tetramethylethylene oxide. The reactions are expressed by the following equations: (1)  $CMe_2Br\cdot CMe_2Br + H_2O = OH\cdot CMe_2\cdot CMe_2\cdot OH + HBr$ ;

(2)  $OH\cdot CMe_2\cdot CMe_2\cdot Br = O\begin{smallmatrix} \swarrow CMe_2 \\ \searrow CMe_2 \end{smallmatrix} + HBr$ ; (3)  $O\begin{smallmatrix} \swarrow CMe_2 \\ \searrow CMe_2 \end{smallmatrix} + H_2O = OH\cdot CMe_2\cdot CMe_2\cdot OH$ .

The action of water on  $\beta$ -methyl- $\beta$ -butylene bromide in presence of lead oxide takes place much less readily than in the preceding case and requires constant shaking of the reacting mixture. The first product of the reaction may be regarded as  $OH\cdot CMe_2\cdot CHMeBr$ , which is resolved into hydrogen bromide and  $\beta$ -methyl- $\beta$ -butylene oxide, 15 per cent. of the theoretical yield of the latter being obtained. Some of the  $\beta$ -methyl- $\beta$ -butylene oxide takes up water, giving the glycol,  $OH\cdot CMe_2\cdot CHMe\cdot OH$ , which is formed in about 20 per cent. yield.

At the ordinary temperature, water acts very slowly on isobutylene bromide in presence of lead oxide, but at 50° the action proceeds somewhat more rapidly, giving 38 per cent. of the theoretical yield of isobutylene glycol; no isobutylene oxide is obtained, as at the temperature at which the reaction is carried out this compound wholly combines with water.

Propylene and ethylene bromides are very slowly attacked by water in presence of lead oxide at 50°.

T. H. P.

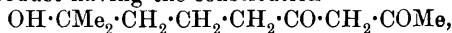
**$\beta$ -Diketones. III.** By GEORGES LESER (*Bull. Soc. Chim.*, 1902, [iii], 27, 64—71. Compare Abstr., 1901, i, 278, 430).—In the present paper, the author describes a number of diketones which he has prepared for the purpose of comparing their properties with those of the diketocyclohexanes previously studied, and with the view of obtaining some light on the tautomeric relationships. Acetylmethylheptanone (*decane- $\beta$ -dione*), obtained by the action of sodium on a

mixture of methylheptanone and ethyl acetate, boils at 117—119° under 20 mm. pressure, and gives a blood-red coloration with ferric chloride. Its copper salt crystallises from alcohol in needles of a fine blue colour. The mol. refraction of the free diketone is 50.9 (calculated for the di-enolic form, 50.4). With hydroxylamine, it yields only one isooxazole, boiling at 126—128° under 27 mm. pressure. By the action of methyl iodide on the sodium salt of the diketone, acetyldimethylheptanone is obtained, which boils at 131—132° under 20 mm. pressure and gives a clear red coloration with ferric chloride; the mol. refraction is 53.8 (calculated for the keto-enolic form, 54.0). It yields an isooxazole which boils at 133—135° under 20 mm. pressure.

*α-Octene-εη-dione*, obtained by the condensation of allylacetone with ethyl acetate in presence of sodium, is a liquid with the odour of garlic, boils at 87—89° under 16 mm. pressure, and has the mol. refraction 41.2 (calculated for the di-enolic form, 40.8). *ζ-Methyl-α-octene-εη-dione*, boils at 97—99° under 10 mm. pressure, and has the mol. refraction 44.2 (calculated for the keto-enolic form, 44.4). Its isooxazole boils at 112—114° under 20 mm. pressure.

Acetylmethylheptenone (*β*-methyl-*β*-nonene-*ζθ*-dione) (compare Abstr., 1899, i, 110) has the mol. refraction 50.9 (calculated for the di-enolic form, 50.0). *Methylacetylmethylheptenone* is a liquid which boils at 127—128° under 10 mm. pressure; it is insoluble in alkalis, and gives a clear red coloration with ferric chloride. Its mol. refraction is 53.65 (calculated for the keto-enolic form, 53.66). It yields an isooxazole boiling at 127—129° under 8 mm. pressure.

Three substances are obtained by the action of sulphuric acid on acetylmethylheptenone: (1) 2-acetyl-1:1-dimethylcyclohexanone-3; (2) a hydration product having the constitution



which boils at 153—154° under 12 mm. pressure; (3) a dehydration product of this substance which boils at 237—238° under normal pressure. On boiling 2-acetyl-1:1-dimethylcyclohexanone-3 with alkalis and condensing the dimethylcyclohexanone formed with ethyl acetate in presence of sodium, 4-acetyl-1:1-dimethylcyclohexanone-3 is obtained isomeric with the first, the acetyl having migrated to position 4; this substance boils at 122—123° under 18 mm. pressure and yields a copper salt which crystallises in greyish-green, silky needles. The diketone is soluble in alkalis and gives a blood-red coloration with ferric chloride (compare Abstr., 1899, i, 743). The mol. refraction of 2-acetyl-1:1-dimethylcyclohexanone is 47.3 (calculated for the keto-enolic form, 47.3), and that of the 4-acetyl-1:1-dimethylcyclohexanone-3 is 48.8 (calculated for the di-enolic form, 48.3).

3-isoButyryl-1-methylcyclopentanone-4, which was obtained by Baeyer and Oehler (Abstr., 1896, i, 247), has the mol. refraction 48.4 (calculated for the di-enolic form, 48.3). Its methyl derivative boils at 108—109° under 8 mm. pressure and has the mol. refraction 51.13 (calculated for the diketonic form, 51.00). It yields a monoxime which melts at 94°.

Propionylacetophenone, obtained by Beyer and Claisen (compare Abstr., 1887, 943), has the mol. refraction 54.4 (calculated for the



di-enolic form, 51.7). Its methyl derivative boils at 165—166° under 10 mm. pressure and has the mol. refraction 57.45 (calculated for the keto-enolic form, 55.36).

The author draws the following conclusions. The mol. refraction of the aromatic  $\beta$ -diketones deviates in an abnormal manner from the value calculated by means of the atomic increments. The non-aromatic  $\beta$ -diketones containing an ethylene linking have a mol. refraction which is appreciably higher than the value calculated for the di-enolic form. The saturated  $\beta$ -diketones, cyclic or open-chained, containing the groups CH and CH<sub>2</sub> respectively between the two carbonyls, have a mol. refraction equal to that calculated for the di-enolic form. Diketones containing no labile hydrogen have the true diketonic form. Unsubstituted, open-chain diketones can yield both dioximes and isooxazoles; those containing only one labile hydrogen atom yield only isooxazoles. Cyclic  $\beta$ -diketones containing one carbonyl group in the nucleus and one in the side chain yield only dioximes, and when the only labile hydrogen atom which they possess is substituted, they yield only monoximes. A. F.

**Isomeric Acetylhalogen Derivatives of Sugars and the Synthesis of Glucosides.** By EMIL FISCHER and E. FRANKLAND ARMSTRONG (*Ber.*, 1902, 35, 833—843. Compare *Abstr.*, 1901, i, 257, 671).—In the preparation of acetylchlorodextroses and the corresponding bromo-compounds, it is not advisable to leave the penta-acetyldextrose in contact with the halogen acid for more than 1½ hours. If liquid hydrogen bromide is allowed to remain in contact with penta-acetyldextrose for 8 days, the product is *triacetyldibromodextrose*, C<sub>12</sub>H<sub>16</sub>O<sub>7</sub>Br<sub>2</sub>, obtained by the replacement of two acetate groups by two bromine atoms. It melts at 176.5° (corr.), may be crystallised from ethyl acetate, and is readily soluble in chloroform or acetone. It reduces Fehling's solution but slightly, and on treatment with methyl alcohol and silver carbonate yields *triacetylmethylglucoside bromohydrin*, C<sub>13</sub>H<sub>19</sub>O<sub>8</sub>Br, crystallising in needles and melting at 126—127° (corr.). This does not reduce Fehling's solution until after hydrolysis with mineral acids, and is readily soluble in benzene, chloroform, or ethyl acetate. The compound described by Skraup and Kreman (*Abstr.*, 1901, i, 506) is identical with  $\beta$ -tetra-acetylchlorogalactose. Both crystallise from ether in long prisms melting at 82—83°, or from light petroleum in needles melting at 76—77°.

$\beta$ -Tetra-acetylbromogalactose, C<sub>14</sub>H<sub>19</sub>O<sub>9</sub>Br, obtained by the action of liquid hydrogen bromide on penta-acetylalactose, crystallises from light petroleum in small prisms melting at 82—83° and has  $[\alpha]_D + 236.4^\circ$  at 20°. Penta-acetylalactose itself has  $[\alpha]_D + 7.48^\circ$ . Tetra-acetyl- $\beta$ -phenolgalactoside, C<sub>20</sub>H<sub>24</sub>O<sub>10</sub>, crystallises from dilute alcohol or from benzene in stout prisms melting at 123—124° (corr.), and has  $[\alpha]_D - 25.77^\circ$  at 20°. When hydrolysed, it yields  $\beta$ -phenolgalactoside melting at 139—141° (corr.) and having  $[\alpha]_D - 39.38^\circ$  at 20°. This galactoside is not hydrolysed by yeast extract, but, like all  $\beta$ -glucosides, is decomposed by emulsin.

Hepta-acetylchloromaltose melts at 66—68°.

Octa-acetylalactose, as obtained by Schmoeger's method (*Abstr.*, 1892,

948), appears to be a mixture; by repeated crystallisation from benzene, the melting point has been raised to  $106^{\circ}$ . On treatment with liquid hydrogen chloride, it is converted into a mixture of two *hepta-acetyl-chlorolactoses*, which may be separated by repeated crystallisation from light petroleum. The one crystallises from this medium in prisms melting at  $57-59^{\circ}$  and has  $[\alpha]_D + 76.2^{\circ}$  at  $20^{\circ}$ . The isomeride, which is insoluble in light petroleum, crystallises in minute prisms melting at  $118-120^{\circ}$  and has  $[\alpha]_D + 73.5^{\circ}$  at  $20^{\circ}$ .

*Tetra-acetylmannitol dichlorohydrin*,  $C_{14}H_{20}O_8Cl_2$ , formed when liquid hydrogen chloride is left in contact with hexa-acetylmannitol for 14 days, melts at  $214^{\circ}$  (corr.) and distils at a higher temperature with only slight decomposition. J. J. S.

**Isolation of Ketoses.** By CARL NEUBERG (*Ber.*, 1902, 35, 959—966).—Secondary asymmetric hydrazines of the type  $R \cdot NPh \cdot NH_2$  can oxidise the group  $-CO \cdot CH_2 \cdot OH$ , but not the group  $-CH(OH) \cdot CHO$ , to the group  $-CO \cdot CHO$ ; they therefore yield osazones with ketoses, but hydrazones with aldoses. Phenylmethylhydrazine was found to be best suited for the purpose, and condenses readily in acetic acid solution with ketoses, forming osazones which mostly crystallise readily from alcohol.

*d-Fructosephenylmethylosazone*, from lævulose, crystallises in long, slender, bright yellow crystals, melts at  $158-160^{\circ}$ , and could not be obtained from dextrose, mannose, or glucosamine.

*d-Fructosephenylbenzylosazone* crystallises in small, felted needles melting at  $190^{\circ}$ , and *d-fructosediphenylosazone* is a similar compound melting at  $167^{\circ}$ .

*d-Arabinketosephenylmethylosazone* crystallises in orange-red needles which soften at  $169^{\circ}$  and melt and decompose at  $172^{\circ}$ .

*Dihydroxyacetonephenylmethylosazone*, obtained from the syrup given by the action of bromine on lead glycerate, crystallises in yellowish needles which melt and evolve gas at  $127-130^{\circ}$ .

*Sorbosephenylmethylosazone* is an oil.

The following example will show how ketoses may be separated from aldoses: a mixture of mannose and lævulose, obtained by the oxidation of *d*-mannitol, when treated with an alcoholic solution of phenylmethylhydrazine, deposits mannosephenylmethylhydrazone, and the filtered solution, when acidified with acetic acid and warmed, yields *d*-fructosephenylmethylosazone.

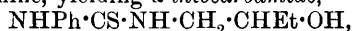
*Dextrosephenylmethylhydrazone* crystallises from alcohol in long, striated plates and melts at  $130^{\circ}$ . R. H. P.

**Rotatory Power of Sucrose; its Variation with Temperature and with the Wave-length of the Light.** By HENRI PELLAT (*Zeit. Ver. deut. Zuckerind.*, 1902, 552, 1—3).—Replies to the criticisms of Schönrock on the author's work on this subject (*Abstr.*, 1901, i, 672). T. H. P.

**Density of Sucrose in Aqueous Solutions.** By A. DEMICHEL (*Ann. Chim. anal.*, 1902, 7, 49—52).—As the result of a mathematical investigation, the author concludes that the supposed liquid

sucrose, having a density of 1.55625 at 15°, does not exist. The figure is only the result of a calculation by a formula the application of which is no longer legitimate when the liquid has become super-saturated.  
L. DE K.

**Amino-alcohols containing C<sub>4</sub> and C<sub>5</sub>.** By RENÉ TORDOIR (*Bull. Acad. roy. Belg.*, 1901, 695—702).—The author communicates the results of a study of the two compounds,  $\alpha\beta$ -butanolamine [ $\alpha$ -amino-sec.butyl alcohol],  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NH}_2$ , and  $\beta$ -aminodiethylcarbinol,  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_3$ . The former is obtained by the reduction of the corresponding nitro-compound, the reduction being best effected by means of aluminium amalgam; it is a colourless liquid, having a disagreeable odour of mice and a sharp taste, boils at 172° under 755 mm. pressure, has the sp. gr. 0.927 at 17° and  $n_D$  1.4772, corresponding with a mol. refraction of 27.11 (calculated, 26.23). It is hygroscopic, and dissolves readily in water with rise of temperature. With benzoyl chloride, it yields a *dibenzoyl* derivative,  $\text{OBz}\cdot\text{CHEt}\cdot\text{CH}_2\cdot\text{NHBz}$ , which melts at 107°. With picrolonic acid, the butanolamine forms a salt which crystallises in yellow, silky needles, decomposes at about 230°, and is very insoluble in water. Phenylthiocarbimide readily combines with the butanolamine, yielding a *thiocarbamide*,



which crystallises from alcohol in small prisms melting at 102°. *Butanolamine oxalate* is a white, amorphous salt which melts at 193°. The *picrate* is a yellow, crystalline salt which decomposes at about 130°. With ethyl oxalate, butanolamine forms a *dihydroxybutyloxamide*,  $\text{C}_2\text{O}_2(\text{NH}\cdot\text{CH}_2\cdot\text{CHEt}\cdot\text{OH})_2$ , which crystallises from alcohol in scales melting at 198°.

*Bi-secondary normal  $\beta\gamma$ -pentanolamine* [ $\beta$ -aminodiethylcarbinol], obtained by the reduction of bi-secondary normal  $\beta\gamma$ -nitropentanol by means of aluminium amalgam, is a colourless liquid with a disagreeable taste and odour, which boils at 174° under 760 mm. pressure, has a sp. gr. 0.911 at 17°,  $n_D$  1.4458, and mol. refraction 30.11 (calculated, 30.07); it is only slightly soluble in water. Its *dibenzoyl* derivative crystallises in scales, insoluble in water but soluble in alcohol or ether, and melts at 122°; the *picrolonate* crystallises in yellow, silky needles, which melt almost without decomposition at 215° (compare Jänecke, *Abstr.*, 1899, i, 476).

Attention is further drawn to the fact that the boiling points of the two amino-alcohols described above are sensibly the same, showing that the introduction of the methyl group does not appreciably affect the volatility.  
A. F.

**Amino-alcohols containing C<sub>4</sub> and C<sub>5</sub>.** By PAUL STIÉNON (*Bull. Acad. roy. Belg.*, 1901, 703—708).— $\alpha\beta$ -Butanolamine [ $\beta$ -aminobutyl alcohol],  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{OH}$ , obtained by the reduction of the corresponding nitro-compound, is a liquid which boils at 172—174° under the ordinary pressure. With oxalic acid, it yields a white, amorphous oxalate which melts at 176°.

*n- $\beta\gamma$ -Pentanolamine* [ $\gamma$ -aminomethylpropylcarbinol],  
 $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CHMe}\cdot\text{OH}.$

obtained by the reduction of the corresponding nitro-compound, is a colourless liquid which boils at  $174^\circ$  under 765 mm. pressure; it has a sp. gr. 0.906 at  $18^\circ$ , and is very slightly soluble in water but readily so in alcohol. With oxalic acid, it yields an acid and a normal salt, the former melting at  $204^\circ$ , the latter at  $166^\circ$ .

The replacement of a hydrogen atom in one of the  $\text{CH}_2$  groups of ethanolamine (b. p.  $171^\circ$ ) by ethyl has no effect on the boiling point, whilst the replacement of the hydrogen by methyl lowers the boiling point about  $10^\circ$ .  
A. F.

**Derivatives of Glucosamine.** By E. ROUX (*Compt. rend.*, 1902, 134, 291—293. Compare Abstr., 1901, i, 372).—On dissolving recently precipitated cupric hydroxide in a 10 per cent. aqueous solution of glucosamine, a blue solution is obtained, from which the compound  $\text{C}_6\text{H}_{11}\text{O}_5\text{NCu}_2$  separates in rectangular plates of a clear blue colour. *Glucosamine picrate* crystallises in chrome-yellow, slender needles melting at  $137^\circ$ . *Glucosamine platinichloride* crystallises in pale yellow prisms melting at  $116$ — $118^\circ$ .

When glucosamine is treated with boiling acetyl chloride, the *hydrochloride* of penta-acetylglucosamine is obtained as a mass of slender needles, which melt at  $170^\circ$  and readily volatilise. With acetic anhydride, glucosamine yields a *hexa-acetyl* derivative, which crystallises in small, hygroscopic leaflets melting at  $70^\circ$  and boiling at about  $250^\circ$ . *Benzylideneglucosamine*,  $\text{C}_6\text{H}_{13}\text{O}_5\text{N}\cdot\text{CHPh}$ , prepared from benzaldehyde and glucosamine, crystallises in long, slender needles melting at  $162$ — $163^\circ$  and decomposed by water. *Glucosaminecarbamide*,  $\text{C}_6\text{H}_{14}\text{O}_5\text{N}\cdot\text{CO}\cdot\text{NH}_2$ , prepared from glucosamine sulphate and potassium cyanate, forms needles, extremely soluble in water, which melt at  $149^\circ$  and have  $[\alpha]_D -12.5^\circ$ . This substance does not reduce Fehling's solution, is hydrolysed by barium hydroxide forming carbon dioxide, ammonia, and glucosamine, with sodium hypobromite gives oxalic acid and the whole of the nitrogen in the form of gas, and with mercuric oxide or mercuric nitrate yields soluble compounds.

Glucosamine and phenylcarbimide in solution in pyridine yield a *phenylcarbamide*,  $\text{C}_6\text{H}_{14}\text{O}_5\text{N}\cdot\text{CO}\cdot\text{NHPh}$ , which crystallises in short needles melting at  $174^\circ$ , and does not evolve nitrogen when treated with sodium hypobromite. With excess of phenylcarbimide, a *penta-phenylcarbamic phenylcarbamide*,  $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5\text{O}_5(\text{CO}\cdot\text{NHPh})_5$ , is obtained; it crystallises in microscopic needles melting and decomposing at  $305^\circ$ , and is not attacked by boiling acids or alkalis. K. J. P. O.

**Betaines.** By RICHARD WILLSTÄTTER (*Ber.*, 1902, 35, 584—620).—The betaines are termed  $\alpha$ ,  $\beta$ ,  $\gamma$ , &c., according to the position of the amino-group. The prefixes also indicate the alkyl and acyl groups present; for example,  $\gamma$ -trimethylbutyrobetaine. The acetylbetaines are, for brevity, simply termed betaines, for example, methyl-diethylbetaine,  $\text{NMeEt}_2\langle\text{CH}_2\text{O}\rangle\text{CO}$ ,

The intramolecular reaction between methyl dimethylaminoacetate and betaine is a reversible one, below  $135^\circ$  both compounds are stable,

between  $135^{\circ}$  and  $293^{\circ}$  the betaine is the stable form, but above  $293^{\circ}$  it is incapable of existence. The esters of other tertiary  $\alpha$ -amino-acids cannot be transformed into betaines in a similar manner; when heated, they yield decomposition products of betaines, namely, tertiary amines. The esters of  $\beta$ - and  $\gamma$ -amino-acids in many cases yield betaines, or their decomposition products, when heated; for example, methyl dimethyl- $\beta$ -aminopropionate and methyl dimethyl- $\gamma$ -aminobutyrate. Methyl dimethylaminoformate may be heated considerably above its boiling point without undergoing decomposition.

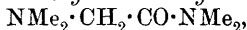
The transformation of betaines into esters of amino-acids occurs in the case of all  $\alpha$ -betaines, but not with the  $\beta$ - and  $\gamma$ -compounds.

When the betaine contains different alkyl groups, it is always the methyl group which passes to the carboxylic group (compare Lossen, *Annalen*, 1876, 181, 377; Lawson and Collie, *Trans.*, 1888, 53, 625; Collie and Schryver, *ibid.*, 1890, 57, 767).

Brühl's statement (this Journal, 1875, 1020; 1876, i, 698) that when triethylglycine is distilled a considerable portion passes over unchanged is incorrect; it gives an almost theoretical yield of ethyl diethylaminoacetate, together with a little triethylamine.

It is thought probable that although amino-acids may have the ammonium constitution (Walker, *Proc.*, 1894, 94, and Sakurai, *ibid.*, 90), yet when they volatilise, it is in the form of the free acid containing a carboxylic group. In no case, however, have two desmotropic modifications been obtained.

*Methyl dimethylaminoacetate*,  $\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$ , is a volatile oil boiling at  $135^{\circ}$  (corr.) or at  $51$ – $52^{\circ}$  under 30 mm. pressure; it does not yield precipitates with platinic chloride or picric acid, and is usually accompanied by *dimethylaminoacetyldimethylamide*,



which distils at  $99$ – $100^{\circ}$  under 34 mm. pressure, and further yields a crystalline *aurichloride*. The *methiodide* of the ester,  $\text{C}_6\text{H}_{14}\text{O}_2\text{NI}$ , crystallises from alcohol in colourless needles melting at  $153.5$ – $154.5^{\circ}$ , or from acetone in long prisms.

Betaine melts and decomposes at  $293^{\circ}$ ; the *aurichloride* melts at  $209^{\circ}$ , Fischer (*Ber.*, 1894, 27, 165) gives  $230$ – $235^{\circ}$ ; the *platinichloride* (Jahns, *Abstr.*, 1893, ii, 485; Liebreich, *Ber.*, 1870, 3, 161) crystallises in large plates containing  $4\text{H}_2\text{O}$ ; in the anhydrous form, it melts and decomposes at  $242^{\circ}$ . The *hydriodide*,  $\text{C}_5\text{H}_{12}\text{O}_2\text{NI}$ , melts at  $188$ – $190^{\circ}$ , and is readily soluble in water or in boiling alcohol. A compound,  $(\text{C}_5\text{H}_{11}\text{O}_2\text{N})_2 \cdot \text{KI} \cdot 2\text{H}_2\text{O}$ , crystallises from alcohol in glistening prisms, and, when anhydrous, melts and decomposes at  $228$ – $229^{\circ}$ .

*Ethyl dimethylaminoacetate* boils at  $149$ – $150^{\circ}$  (corr.), and is soluble in cold water, the *ethiodide* crystallises in short prisms melting at  $71.5$ – $72.5^{\circ}$ .

*Methyl diethylaminoacetate* boils at  $163.5^{\circ}$  (corr.), is miscible with cold water in all proportions, but is only sparingly soluble in warm water; it yields a crystalline *aurichloride*, and a *methiodide* melting at  $90$ – $92^{\circ}$ .

*Dimethylaminodimethylacetal*,  $\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OMe})_2$ , is a colourless, mobile liquid boiling at  $137.5^{\circ}$  (corr.), is miscible with water in all pro-

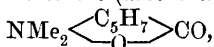
portions, and has no reducing properties (Störmer and Prall, Abstr., 1897, i, 457).

*Dimethylethylbetaine*,  $\text{NMe}_2\text{Et} \langle \text{CH}_2 \rangle \text{CO}$ , obtained by the action of silver oxide on the ethiodide of ethyl dimethylaminoacetate, crystallises from alcohol in four-sided plates melting and decomposing at  $229-231^\circ$ . The *platinichloride* is readily soluble, and the *aurichloride* crystallises in prisms decomposing at  $236-237^\circ$ . When the betaine is heated at  $240-245^\circ$ , it is transformed into *methyl methylethylaminoacetate* boiling at  $151-152^\circ$  (corr.). *Copper methylethylaminoacetate*,  $\text{C}_{10}\text{H}_{20}\text{O}_4\text{N}_2\text{Cu}, 3\text{H}_2\text{O}$ , crystallises in deep blue, four-sided plates.

*Methyldiethylbetaine* crystallises in prisms containing  $1\text{H}_2\text{O}$ ; in the anhydrous form, it melts at  $133-135^\circ$ .

*Methyl  $\beta$ -dimethylaminopropionate*,  $\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$ , distils at  $154.5^\circ$ , forms a sparingly soluble *picrate*, a crystalline *aurichloride*, and a *methiodide* crystallising in plates or prisms and melting and decomposing at  $191-192^\circ$ . When warmed with alkalis, the methiodide yields acrylic acid and trimethylamine; with silver oxide, it gives  *$\beta$ -trimethylpropiobetaine*,  $\text{NMe}_2 \langle \text{CH}_2 \cdot \text{CH}_2 \rangle \text{CO}$ , in the form of glistening needles containing  $1\text{H}_2\text{O}$ ; when quickly heated, it melts and decomposes at  $126^\circ$ , but when slowly heated decomposes gradually at about  $100^\circ$ , the products formed being trimethylamine and acrylic acid. The *hydrochloride* crystallises in four-sided plates melting at  $195-196^\circ$ , the *aurichloride* crystallises in golden-yellow prisms melting and decomposing at  $197-198^\circ$ , and only sparingly soluble in water.

*Dimethyltetrahydronicotinobetaine (arecaidinmethylbetaine)*,



obtained from arecoline methiodide (Willstätter, Abstr., 1897, i, 385), crystallises in colourless, compact prisms containing  $2\text{H}_2\text{O}$  and, when anhydrous melts and decomposes at  $248^\circ$ . The *platinichloride* and *aurichloride* both crystallise in plates. When the betaine is heated at  $240^\circ$ , it yields a base  $\text{C}_7\text{H}_{13}\text{N}$ , the *platinichloride* of which crystallises in pale red prisms melting at  $116-118^\circ$ , and the *aurichloride* in bronzy-yellow plates melting at  $66-67^\circ$ .

*Methyl  $\gamma$ -dimethylaminobutyrate*,  $\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$ , is a colourless oil distilling at  $171.5-173^\circ$  (corr.), and yields a crystalline *picrate* and *aurichloride*.

*$\gamma$ -Trimethylbutyrobetaine*,  $\text{NMe}_2 \langle \text{CH}_2 \cdot \text{CH}_2 \rangle \text{CH}_2$ , crystallises in colourless plates containing  $3\text{H}_2\text{O}$ ; in the anhydrous state, it begins to soften at  $130^\circ$  and decomposes at  $222^\circ$ . The *platinichloride* melts and decomposes at  $224-225^\circ$ , and the *aurichloride* crystallises in long, glistening needles. When heated, the betaine decomposes into trimethylamine and butyrolactone, as does also methyl  $\gamma$ -dimethylaminobutyrate at  $205-225^\circ$ .  
J. J. S.

**Serine and isoSerine.** By EMIL FISCHER and HERMANN LEUCHS (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 78-87).—Serine, identical

with that obtained from silk, is produced by allowing a mixture (in mol. proportions) of glycollic aldehyde and ammonia in alcoholic solution to stand for 24 hours, then adding the calculated quantity of hydrocyanic acid; after some time, an equal volume of hydrochloric acid is added, and 24 hours thereafter the cooled solution is saturated with hydrogen chloride. Ammonium chloride is removed by filtration, and the ammonia and chlorine by means of lead oxide; dissolved lead is removed from the filtrate by hydrogen sulphide and the filtrate evaporated in a vacuum, and then precipitated with alcohol. The crystals become brown at 225° and melt, with decomposition, at 246° (corr.). The solubility of the synthetical serine in water at 20° is 1 : 23·13.

*Serine phenylcarbimide* was prepared by the action of phenylcarbimide on serine in alkaline solution. It can be crystallised from hot water, melts at 168—169° (corr.), and is extremely easily soluble in alcohol.

When reduced with hydriodic acid, serine gives  $\alpha$ -alanine. The synthesis and reduction indicate that serine is  $\alpha$ -amino- $\beta$ -hydroxypropionic acid.

*isoSerine* is obtained by heating  $\beta$ -chlorolactic acid with ammonia at 130°. *isoSerine* becomes brown at about 238° and melts, with decomposition, at 248° (corr.). The composition of the copper salt is  $C_3H_5O_3NCu_3H_2O$ , and it is probable that the alcoholic hydroxyl group plays a part in the formation of this.

*isoSerine phenylcarbimide* melts at 183—184° (corr.). It is easily soluble in alcohol, but almost insoluble in ether. When reduced with hydriodic acid, it gives  $\beta$ -alanine, so that *isoserine* is  $\beta$ -amino- $\alpha$ -hydroxypropionic acid.

Aldol-ammonia, when treated with hydrocyanic acid, gives  $\alpha$ -amino- $\gamma$ -hydroxyvaleric acid, which is soluble in hot water, has a sweet taste, and melts at 212°.

The authors purpose further to apply this method of Strecker's for the synthesis of  $\alpha$ -amino-acids from hydroxyaldehydes. J. McC.

**Action of Sulphuryl Chloride on Urethane.** By FRITZ EPHRAIM (*Ber.*, 1902, 35, 776—782).—A 25 per cent. yield of ethyl allophanate is obtained when urethane is treated with sulphuryl chloride in benzene solution. *Sulphourethane*,  $SO_2[O\cdot C(OEt)\cdot NH]_2$ , obtained when the sodium derivative of urethane in benzene solution is treated with sulphuryl chloride, crystallises well from alcohol, melts at 171°, and forms crystalline *sodium* and *potassium* derivatives. When a boiling solution of urethane in benzene is treated with sodium, the *sodium* derivative of sodium allophanate,  $NH_2\cdot C(ONa)\cdot N\cdot CO_2Na$ , is obtained; this forms star-shaped masses of crystals and is completely decomposed when treated with acids. Sulphuryl chloride seems to have no action on nitrourethane or aminosulphonic acid. R. H. P.

**Action of Ammonia on Esters of Alkylmalonic Acids.** By EMIL FISCHER and ALFRED DILTNEY (*Ber.*, 1902, 35, 844—856).—The ethyl esters of malonic and of monoalkylated malonic acids react with both liquid and alcoholic ammonia, yielding the corresponding amides, and forming esters of malonamic acids as intermediate products. Esters

of dialkylated malonic acids, on the other hand, yield either no amide or only minute traces. The compound described by Thorne (*Trans.*, 1881, 39, 545) as dimethylmalonamide is, in reality, monomethylmalonamide; it melts at  $216.5^{\circ}$  (corr.), and not at  $207^{\circ}$  as stated by Henry (*Jahresbericht*, 1889, 639). *Ethyl methylmalonamide*,



sublimes in colourless needles melting at  $72.5^{\circ}$ , and is readily soluble in water or alcohol.

Ethylmalonamide (Freund and Goldschmidt, *Abstr.*, 1888, 675; Henry, *loc. cit.*) melts at  $216^{\circ}$  (corr.). *Ethyl ethylmalonamide* sublimes in colourless needles and melts at  $77^{\circ}$  (corr.). Propylmalonamide (Henry, *loc. cit.*) melts at  $184^{\circ}$  (corr.). *Ethyl propylmalonamide* crystallises in needles melting at  $101^{\circ}$  (corr.).

Ethyl dimethylmalonate yields only 2.6 per cent. of amide when heated at  $145^{\circ}$  for 30 hours with alcohol saturated with ammonia at  $0^{\circ}$ .

The amides of dialkylated malonic acids cannot be obtained from the corresponding ammonium salts, since when these are heated dialkylacetamides are produced. They may, however, be obtained by the action of ammonia on the acid chlorides (compare Franchimont, *Abstr.*, 1886, 448).

*Diethylmalonamide*,  $\text{CEt}_2(\text{CO}\cdot\text{NH}_2)_2$ , crystallises from boiling water in prisms melting at  $224^{\circ}$  (corr.) and is practically insoluble in ether. *Dipropylmalonamide*, obtained from the chloride, which boils at  $221\text{--}223^{\circ}$ , crystallises in long needles and melts at  $214^{\circ}$  (corr.). *Dimethylmalonamide* melts at  $261^{\circ}$  (corr.).

Ethyl phenylacetate yields an amide much more readily than ethyl benzoate.

Ethyl trimethylacetate does not react with ammonia to yield an amide.

Malonamide, propylmalonamide, and diethylmalonamide have been hydrolysed with sodium hydroxide; the amounts decomposed after boiling for 42 minutes were respectively 89, 57, and 3 per cent. Dimethylmalonamide is much more readily hydrolysed than diethylmalonamide.

J. J. S.

**Production of the Imides of Succinic and Glutaric Acids by the Partial Hydrolysis of the Corresponding Nitriles.** By MARSTON T. BOGERT and DAVID C. ECCLES (*J. Amer. Chem. Soc.*, 1902, 24, 20—25).—When succinonitrile (2 mols.) is heated in a sealed tube with water (4 mols.) and sulphuric acid (1 mol.), a brown, crystalline product is obtained, which consists of a mixture of  $\beta$ -cyanopropionic and succinic acids and their amides, succinamic acid, succinimide, ammonium sulphate, and unchanged succinonitrile. The best yield of succinimide is obtained by heating for about 2 days at  $165\text{--}175^{\circ}$ . If the nitrile (1 mol.) is heated with water (2 mols.) in the absence of sulphuric acid for 5 hours at  $153\text{--}173^{\circ}$ , very little imide is produced and most of the nitrile remains unaltered. When the nitrile (1 mol.) is heated with water (1 mol.) for 6 hours at  $153\text{--}173^{\circ}$ , a large quantity of succinimide is formed, together with a small amount of succinamic acid, traces of succinamide, but no cyanopropionamide.



If glutaronitrile (2 mols.) is heated in a sealed tube with water (4 mols.) and sulphuric acid (1 mol.) for 5—10 hours at 155—200°, glutarimide is obtained in a yield of 60 per cent., but no amide or amic acid can be detected.

E. G.

**Thiuram Disulphides and isoThiuram Disulphides. I.** By JULIUS VON BRAUN (*Ber.*, 1902, 35, 817—830. Compare Abstr., 1900, i, 644).—It is shown that alkylammonium salts of alkylated dithiocarbamic acids on oxidation with iodine, bromine, hydrogen peroxide, or potassium persulphate, readily yield thiuram disulphides, for example,  $R^1 \cdot NH \cdot CS \cdot SH \cdot NH_2 R^2 + I_2 = S_2(CS \cdot NHR^1)_2 + 2NH_2 R^2 \cdot HI$ .

*Tetramethylthiuram disulphide*,  $S_2(CS \cdot NMe_2)_2$ , prepared by oxidising an alcoholic solution of dimethylamine dimethylthiocarbamate, forms small, white crystals melting at 146°. *Tetrapropylthiuram disulphide*,  $S_2(CS \cdot NPr^a)_2$ , is obtained by oxidising the corresponding dithiocarbamate and melts at 50°.

*Diphenyldimethylthiuram disulphide*,  $S_2(CS \cdot NMePh)_2$ , prepared by adding iodine to an alcoholic solution of mol. proportions of methylaniline and carbon disulphide, melts at 198°. The corresponding *diethyl* compound is prepared by oxidising a mixture of ethylaniline and carbon disulphide with hydrogen peroxide; it melts at 169—170°.

Dimethyl- and diethyl-thiuram disulphides (m. p. 102° and 75°) can similarly be obtained from an alcoholic solution of the base and carbon disulphide; the following hitherto undescribed dialkylthiuram disulphides have also been prepared; *dipropylthiuram disulphide*,  $S_2(CS \cdot NHPr^a)_2$ , melting at 58°; *diisopropylthiuram disulphide*, melting at 69°; *düsobutylthiuram disulphide*, melting at 51°; *diisoamylthiuram disulphide*, melting at 61—62°; *dibenzylthiuram disulphide*, melting at 71°. These dialkylthiuram disulphides readily decompose into the corresponding thiocarbimides, hydrogen sulphide, and sulphur on the one hand, or, on the other hand, into thiocarbamides, carbon disulphide, and sulphur. With the more simple alkyl groups, the first decomposition is more prominent; with the more complex alkyl groups, the second decomposition mainly occurs.

The neutral dialkylthiuram disulphides are converted by alcoholic potash into isomeric *isothiuram* compounds, which are acid in character, and form a series of metallic salts.

*S-Dimethylisothiuram disulphide*,  $S_2[C(SMe) \cdot NH]_2$ , is obtained when methyl iodide acts on thiuram disulphide dissolved in alcohol containing sodium ethoxide; it is also formed by the action of alcoholic sodium hydroxide on the isomeric dimethylthiuram disulphide; it crystallises in colourless needles from benzene, melting at 85°. With concentrated acids, methyl mercaptan is formed.

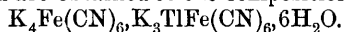
*N-Dimethyl-S-dimethylisothiuram disulphide*,  $S_2[C(SMe) \cdot NMe]_2$ , prepared from dimethylthiuram disulphide, is a liquid boiling at 100° under 12 mm. pressure. *N-Dibenzyl-S-dipropylisothiuram disulphide*,  $S_2[C(SPr^a) \cdot N \cdot CH_2Ph]_2$ , prepared from dibenzylthiuram disulphide and propyl bromide, is a pale red liquid, boiling at 175° under 12 mm. pressure.

With iodine, the salts of *isothiuram* disulphides yield quantitatively sulphur and alkylthiocarbimides.

The mechanism of the reactions by which the substances described in this paper are produced, are fully discussed. K. J. P. O.

**Ferric Ferrocyanide.** By J. MATUSCHEK (*Chem. Zeit.*, 1902, 26, 41—43. Compare Abstr., 1901, i, 262, 454, 635, 677).—By the action of oxalic acid on potassium ferrocyanide, with access of oxygen, blue precipitates are obtained which have the composition of Prussian blue but exhibit a coppery lustre, and are therefore to be designated as Paris blue. The blue precipitate is not produced in the dark, and temperature, as well as the concentration of the solutions, has an influence on the formation of the precipitate. A. F.

**Double Cyanides of Thallium.** By TH. FISCHER and R. BENZIAN (*Chem. Zeit.*, 1902, 26, 49—50).—*Thallium ferrocyanide.* On adding a hot concentrated solution of thallous sulphate to potassium ferrocyanide and allowing the mixture to cool, the yellow, crystalline double salt,  $\text{Tl}_4\text{Fe}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$  is obtained. It is sparingly soluble in cold, more readily in hot, water (compare Crookes, *Chem. News*, 1861, 3, 303). From the aqueous solution, hydrochloric acid precipitates thallous chloride; potassium iodide, thallous iodide; baryta water, barium ferrocyanide; and silver nitrate, silver ferrocyanide. Alkalis and dilute nitric and sulphuric acids have no action on the aqueous solution of the thallium ferrocyanide, but concentrated acids decompose it. By mixing dilute solutions of potassium ferrocyanide and thallous sulphate, precipitating with alcohol and recrystallising the precipitate from water, yellow plates are obtained of the composition



This salt is isomorphous with potassium ferrocyanide, and behaves towards reagents like thallium ferrocyanide, but is more soluble in cold water.

*Thallium ferricyanide.* On adding thallous sulphate to a solution of potassium ferricyanide, a dark red solution is obtained from which, on concentration in a vacuum, red needles having the composition  $\text{K}_2\text{TlFe}(\text{CN})_6$  separate. This salt is decomposed by pure water, but the decomposition is prevented by the presence of potassium ferricyanide, and from the solution containing the latter salt red prisms of the composition  $4\text{K}_3\text{Fe}(\text{CN})_6 \cdot 3\text{K}_2\text{TlFe}(\text{CN})_6$  are deposited on evaporation. Double salts of the composition  $\text{Tl}_5\text{KFe}_2(\text{CN})_{12}$ , and mixtures of  $\text{K}_2\text{Tl}_4\text{Fe}_2(\text{CN})_{12}$  and  $\text{K}_3\text{Tl}_3\text{Fe}_2(\text{CN})_{12}$ , are obtained by employing thallium phosphate instead of thallous sulphate. *Thallium chromicyanide* is obtained in bright yellow, anhydrous plates by heating thallous sulphate with excess of basic lead chromicyanide and concentrating the solution in a vacuum over sulphuric acid. It has the composition  $\text{Tl}_3\text{Cr}(\text{CN})_6$ . On shaking a warm concentrated solution of potassium chromicyanide with thallous cyanide and concentrating the resulting solution in a vacuum, bright yellow crystals of the composition  $\text{K}_2\text{TlCr}(\text{CN})_6$  are obtained which are isomorphous with those of potassium chromicyanide. Both these chromicyanogen compounds are soluble in water. *Thallium cobalticyanide* is obtained by neutralising an aqueous solution of hydrocobalticyanic acid with thallous hydroxide and concentrating the solution in a vacuum. It has the composition  $\text{Tl}_3\text{Co}(\text{CN})_6$ , and shows all the properties of the salt as described by Fronsmüller (Abstr., 1878, 395). The salt is fairly

readily soluble in hot 50 per cent. alcohol, and crystallises out almost completely on cooling. A potassium thallium salt of the composition  $K_3Tl_3Co(CN)_{12}$  is obtained by mixing hot concentrated solutions of potassium cobaltcyanide and dibasic thallous phosphate. It is much more readily soluble in cold water than thallium cobaltcyanide. A. F.

**Dichloro-acetyl Phosphide.** By P. N. EVANS and C. E. VANDERKLEED (*Amer. Chem. J.*, 1902, 27, 142—146).—Dry hydrogen phosphide was passed into dichloro-acetyl chloride for some hours. After some time, a large quantity of ether was added and a gummy mass was precipitated which gradually solidified to a faintly yellow powder. Analysis showed that the powder has the formula  $CHCl_2 \cdot CO \cdot PH_2$ . It chars without melting at  $200^\circ$  and is insoluble in ether, benzene, or chloroform, but very easily soluble in alcohol. It is slowly decomposed by water with evolution of hydrogen phosphide. J. McC.

**Composition of Norwegian Wood Tar.** By J. ALFRED MJØEN (*Zeit. angew. Chem.*, 1902, 15, 97—111).—Various wood tars have been investigated, namely: I, Norwegian retort tar, obtained by distillation of pinewood sawdust; II, a tar obtained by peasants in Gudbrandsdalen; III, Austrian beech-wood tar; IV, Bohemian pine-wood tar. The tar was in each case treated as far as possible under conditions not favourable to chemical change, for example, all distillations were carried on under reduced pressure, and as far as possible in absence of air, and the various fractions obtained were kept in the dark.

	I.	II.	III.	IV.	
Aqueous solution .....	4.45	5	7.2	3.7	per cent.
Acetone .....	0.4	0.07	—	—	"
Total aldehydes and ketones	0.8	0.5	—	—	"
Acetic acid .....	0.36	0.37	—	—	"
Total fatty acids.....	3.64	1.78	{Acetic, propionic, butyric, and valeric were detected.		
Guaiacol and creosote... ..	{creosote 20.0		{guaiacol {creosote 10.5 { 7.5		per cent.
Phenols and phenolic deriva- tives .....	44.7	21.5	41.0	17.0	"
Retene.....	none	4—5	—	—	"
Pitch .....	20.6	10.1	21.0	29.0	"
Hydrocarbons and neutral substances .....	22.5	*46.0	18.0	40.0	"
Esters .....	—	1.4	—	—	"
Alcohols .....	1.0	—	—	—	"

\* About 20 per cent. aliphatic and 80 per cent. aromatic hydrocarbons.

Nitrogen and sulphur compounds were not present, but certain unsaturated compounds were isolated.

The retort tar has a characteristic unpleasant odour quite different from that of the Finnish tar largely used in Norway, and also differs from the latter in the relatively large amounts of soluble fatty acids present. J. J. S.

**Stereochemistry of Benzene.** By WILHELM MARCKWALD (*Ber.*, 1902, **35**, 703).—In reference to Graebe's discussion on the space formula of benzene (compare this vol., i, 209) the author states that all those configurations which do not contain the centres of gravities of their constituent atoms in the same plane may be *a priori* excluded on purely stereochemical grounds. G. T. M.

**Action of Bromine on Durene and Penta- and Hexa-methylbenzenes.** By ANTON VON KORCZYNSKI (*Ber.*, 1902, **35**, 868—872).—The influence of sunlight in facilitating the entry of bromine into the side chain is not observable in the case of the higher methylbenzenes. Hexamethylbenzene is not attacked by bromine in sunlight, whilst pentamethylbenzene and durene yield substitution derivatives; in the dark, durene yields a mixture of mono- and dibromo-durene and in sunlight monobromodurene only.

On passing bromine vapour into durene at 100°, substitution in the side chain occurs; a small quantity (about 7 per cent.) of a *durylene dibromide*,  $C_6H_2Me_2(CH_2Br)_2$ , crystallising from alcohol in white needles and melting at 157° was isolated. It was converted by alcoholic potassium acetate into *durylene diacetate*,  $C_6H_2Me_2(CH_2\cdot OAc)_2$ , which crystallises from alcohol in thin, iridescent leaflets and melts at 65°; *durylene glycol*,  $C_6H_2Me_2(CH_2\cdot OH)_2$ , forms thin, white scales, melts at 74°, and on oxidation with aqueous potassium permanganate yields a *xylenedicarboxylic acid* crystallising from alcohol in leaflets and melting at 123° W. A. D.

***p*-Nitrobenzenesulphonic Acid.** By ALFRED EKBOM (*Ber.*, 1902, **35**, 651—656. Compare Blanksma, *Abstr.*, 1901, 461).—Limpricht's statements (this Journal, 1875, 1027) with regard to *p*-nitrobenzenesulphonic acid are incorrect; its chloride is not a liquid, but separates from light petroleum in monoclinic crystals [ $a:b:c = 1.3042:1:1.1369$ ;  $\beta = 74^\circ 21'$ ] melting at 79.5—80.5°, whilst the amide forms monoclinic prisms [ $a:b:c = 0.6501:1:0.5184$ ;  $\beta = 79^\circ 48'$ ] and melts at 177—178°, not at 131°.

On heating the sulphonic chloride with hydriodic acid of sp. gr. 1.5, it is converted into Willgerodt's *p*-dinitrodiphenyl disulphide (*Abstr.*, 1885, 519), which melts at 180—181°, not at 168—170° as stated by Leuckart (*Abstr.*, 1890, 604); the structure of the acid is thus established. Potassium *p*-nitrobenzenesulphonate, obtained from the pure sulphonic chloride, crystallises in prismatic scales with  $1H_2O$ , and is not anhydrous as stated by Limpricht. W. A. D.

***p*-Halogen-arylthiosulphonates.** By JULIUS TROEGER and F. HURDELBRINK (*J. pr. Chem.*, 1902, [ii], **65**, 82—90).—When iodobenzene is heated with fuming sulphuric acid and the product treated with solution of sodium chloride, sodium *p*-iodobenzenesulphonate is produced together with some 1:4-di-iodobenzene. By the action of phosphorus pentachloride on sodium *p*-iodobenzenesulphonate, *p*-iodobenzenesulphonic chloride is obtained, and is converted by potassium sulphide into *potassium p-iodothiobenzenesulphonate*. This salt was not obtained pure, but was converted into the *aniline* salt, which forms a

white, amorphous precipitate and melts at  $138^{\circ}$ . The *benzidine* salt,  $C_6H_4I \cdot S \cdot SO_2H \cdot C_{12}H_8(NH_2)_2$ , forms small crystals, and melts and decomposes at  $204-206^{\circ}$ .

*p-Iodobenzenesulphinic acid*,  $C_6H_4I \cdot SO_2H$ , obtained by the action of hydrochloric acid on potassium *p*-iodothiobenzenesulphonate, melts at  $137^{\circ}$  and dissolves readily in ether or alcohol and sparingly in water; its *sodium* salt crystallises with  $4H_2O$ . By the action of iodine on this sodium salt, *p-iodobenzenesulphonic iodide*,  $C_6H_4I \cdot SO_2I$ , is produced, which crystallises in small, golden-yellow leaflets and melts at  $95^{\circ}$ ; it is converted by ammonia into *p-iodobenzenesulphonamide*. When *p-iodobenzenesulphinic acid* is heated with water in a sealed tube for 8 hours at  $130^{\circ}$ , *p-iodobenzene disulphoxide*,  $(C_6H_4I \cdot SO)_2$ , is obtained, which crystallises in white leaflets, melts at  $193^{\circ}$ , and is readily soluble in alcohol or ether.

The *potassium* salt of *p-bromobenzenethiosulphonic acid*, prepared from *p-bromobenzenesulphonic chloride* and potassium sulphide, was not obtained pure, but was converted into the *p-phenylenediamine* salt,  $(C_6H_4Br \cdot SO_2 \cdot SH)_2 \cdot C_6H_4(NH_2)_2$ , which melts and decomposes at  $155^{\circ}$ ; the *aniline* salt was also prepared.

*Sodium p-chlorobenzenethiosulphonate*,  $C_6H_4Cl \cdot SO_2 \cdot SNa \cdot 2H_2O$ , was obtained by the action of sodium sulphide on *p-chlorobenzenesulphonic chloride*; the *p-phenylenediamine* salt crystallises in needles; the *benzidine* salt was also prepared. E. G.

**Thiocarbimides and Thiocarbamides derived from Terpenes.** By JULIUS VON BRAUN and K. RUMPF (*Ber.*, 1902, 35, 830—833).—Methylcyclohexylamine, camphylamine, pinylamine, thujylamine, and *l*-menthylamine readily combine with carbon disulphide, yielding dithiocarbamates, which on oxidation (*Abstr.*, 1900, i, 644) yield liquid disulphides. When heated, these disulphides are decomposed into sulphur, carbon disulphide, and dialkylthiocarbamides, or, when treated with iodine, they yield the corresponding thiocarbimides which combine with the original bases forming dialkylthiocarbamides.

*Methylcyclohexylthiocarbimide*,  $C_7H_{13} \cdot N : CS$ , boils at  $115.5^{\circ}$  under 13 mm. pressure and reacts with aniline, yielding phenylmethylcyclohexylthiocarbamide melting at  $92^{\circ}$ . *Dimethylcyclohexylthiocarbamide* melts at  $119^{\circ}$ . Camphylthiocarbimide (Goldschmidt and Schulhof, *Abstr.*, 1886, 557) boils at  $160^{\circ}$  under 25 mm. pressure. *Dicamphylthiocarbamide* is an oil. *Pinylthiocarbimide* boils at  $142-143^{\circ}$  under 14 mm. pressure, and *dipinylthiocarbamide* melts at  $189^{\circ}$ . *Thujylthiocarbimide* boils at  $126-128^{\circ}$  under 14 mm. pressure. *Thujylphenylthiocarbamide* melts at  $107-108^{\circ}$ . *Menthylthiocarbimide* distils at  $138^{\circ}$  under 12 mm. pressure, and *dimenthylthiocarbamide* melts at  $200^{\circ}$ . J. J. S.

**Oxidation of Methyl- and Ethyl-aniline.** By EUGEN BAMBERGER and MICHAEL VUK (*Ber.*, 1902, 35, 703—714. Compare *Abstr.*, 1900, i, 435; 1901, i, 200, 587).—When oxidised with hydrogen peroxide, methylaniline yields a mixture of nitrobenzene, azobenzene, and azoxybenzene; this oxidation proceeds so slowly that the intermediate products undergo further changes before the reaction is complete, and the sub-

stances isolated represent only the final stage of the process. The use of Caro's reagent, persulphuric acid, brings about a more rapid oxidation and permits of the isolation of the intermediate products. The secondary base is suspended in water or in ether and treated with a neutralised solution of Caro's reagent at 0—8°; formaldehyde, nitroso-benzene, nitrobenzene, azobenzene, azoxybenzene,  $\beta$ -phenylhydroxylamine,  $\beta$ -methylenebis- $\beta$ -phenylhydroxylamine,  $\text{CH}_2(\text{NPh}\cdot\text{OH})_2$ , and diphenylhydroxyformamidine,  $\text{NPh}\cdot\text{CH}\cdot\text{NPh}\cdot\text{OH}$ , have been identified with certainty, whilst the product also contains a substance having the properties of  $\beta$ -formylphenylhydroxylamine,  $\text{CHO}\cdot\text{NPh}\cdot\text{OH}$ . In all probability, the methylaniline is first oxidised to  $\beta$ -phenylmethylhydroxylamine,  $\text{NMePh}\cdot\text{OH}$ , which, however, is not isolated, but undergoes further oxidation either into  $\beta$ -formyl- $\beta$ -phenylhydroxylamine or  $\beta$ -phenylhydroxylamine. In the second stage of the oxidation, formaldehyde is liberated, and a portion of this compound reacts with  $\beta$ -phenylhydroxylamine yielding  $\beta$ -methylenebis- $\beta$ -phenylhydroxylamine; the methylene compound subsequently loses water, giving rise to diphenylhydroxyformamidine. Nitrobenzene, nitrosobenzene, and azoxybenzene result from the further oxidation of  $\beta$ -phenylhydroxylamine, whilst this hydroxylamine derivative probably condenses with methylaniline to furnish azobenzene; the methyl alcohol, which should result from this interaction, has, however, not been isolated.

Ethylaniline, when oxidised with hydrogen peroxide, yields azobenzene, azoxybenzene, and nitrobenzene, together with a small quantity of a substance having the characters of an aminophenol. With Caro's reagent, the secondary amine gives rise to nitrobenzene, nitrosobenzene, azobenzene, and azoxybenzene.

A small amount of an acidic substance, which corresponds in properties with  $\beta$ -acetyl- $\beta$ -phenylhydroxylamine, is simultaneously produced.

Methylaniline and nitrosobenzene, when condensed in cold glacial acetic acid, yield a mixture of aniline, azobenzene, and azoxybenzene.

G. T. M.

**Oxidation of Methylenebisaniline.** By EUGEN BAMBERGER and FRED. TSCHIRNER (*Ber.*, 1902, 35, 714—730. Compare preceding abstract).—The oxidation of methylenebisaniline,  $\text{CH}_2(\text{NHPh})_2$ , with Caro's acid shows that the reaction involves a partial hydrolysis of the diamine into aniline and formaldehyde, each of these substances having been isolated in the final product; the former, however, is partially oxidised to azoxybenzene, nitrobenzene, and nitrosobenzene, and the latter to formic acid and carbon dioxide.

Anhydro-*p*-hydroxylaminobenzyl alcohol is also a product of this reaction and results from the simultaneous oxidation and hydrolysis of the methylene base.

Oxidation of the methylene base without hydrolysis leads to the production of diphenylformamidine,  $\text{NPh}\cdot\text{CH}\cdot\text{NHPh}$ , and diphenyl *N*-hydroxyformamidine,  $\text{NPh}\cdot\text{CH}\cdot\text{NPh}\cdot\text{OH}$ ; the latter of these amines, by hydrolysis and intramolecular transformation, gives rise to *p*-nitrophenol, a trace of the ortho-isomeride being simultaneously produced. Substances having properties resembling those of *p*-aminobenzaldehyde and  $\beta$ -formyl-

$\beta$ -phenylhydroxylamine are found amongst the products of oxidation, but the compounds themselves have not been isolated.

Diphenylhydroxyformamidine is first isolated in the form of its hydrate,  $\text{NPh}\cdot\text{CH}\cdot\text{NPh}\cdot\text{OH}\cdot\text{H}_2\text{O}$ , melting indefinitely at  $94-95^\circ$ ; the anhydrous base is obtained by drying the hydrate over concentrated sulphuric acid in a vacuum. The *hydrochloride*, *nitrate*, and *copper* compound,  $\text{Cu}(\text{O}\cdot\text{NPh}\cdot\text{CH}\cdot\text{NPh})_2$ , are derivatives of the anhydrous base; the acid salts crystallise in silky needles and the metallic derivative separates from its solution in the ordinary organic solvents in light red, felted needles melting at  $240-241^\circ$ . G. T. M.

**Oxidation of Benzylaniline.** By RUDOLF HÜBNER (*Ber.*, 1902, 35, 731. Compare preceding abstracts).—Benzylaniline, when treated with Caro's reagent in neutral solutions, yields nitrosobenzene, nitrobenzene, azoxybenzene, and benzoic acid. G. T. M.

**Isomerism of Quaternary Ammonium Bases.** By ARTHUR HANTZSCH and ARTHUR HORN (*Ber.*, 1902, 35, 883—888).—Wedekind's isomeric  $\alpha$ - and  $\beta$ -salts of phenylbenzylmethylallylammonium (*Abstr.*, 1899, i, 351; 1900, i, 155) were examined in order to ascertain whether they differed structurally, and especially whether one of them might contain an *isoallyl* or *propyl*, in place of an *allyl*, group; both substances were found, however, to be unsaturated towards bromine and permanganate, and to yield formic, and not acetic, acid on oxidation with 33 per cent. nitric acid. T. M. L.

**Simple and Double Dissociation of Quaternary Ammonium Salts.** By EDGAR WEDEKIND [and, in part, F. OBERHEIDE] (*Ber.*, 1902, 35, 766—776. Compare *Abstr.*, 1900, i, 155, and Pope and Harvey, *Trans.*, 1901, 79, 831).—Ethyl phenyldimethylammoniumiodoacetate (*Abstr.*, 1901, i, 640) crystallises in the rhombic system [ $a:b:c=0.9222:1:0.6912$ ]; the corresponding *methyl* ester separates from alcohol in small, yellow, triclinic crystals, which melt at  $104-105^\circ$ ; either ester, when heated in an oil-bath at  $130^\circ$  for three-quarters of an hour, yields phenyltrimethylammonium iodide. *Methyl p-tolyldimethylammoniumiodoacetate*, prepared from dimethyl-*p*-toluidine and methyl iodoacetate, separates from water in monoclinic crystals [ $a:b:c=1.8080:1:1.1878$ ,  $\beta=84.43^\circ$ ], which soften at  $120^\circ$ , melt and decompose at  $124-125^\circ$ , and, when heated, yield *p-tolyltrimethylammonium iodide*; this crystallises from alcohol and volatilises at  $216-220^\circ$ . Ethyl methyl-tetrahydroquinoliniumiodoacetate, when heated at  $120^\circ$ , yields *dimethyl-tetrahydroquinolinium iodide*, which crystallises in small, colourless prisms melting at  $176^\circ$ ; by silver oxide, the iodide is converted into the *base*, which forms a *platinichloride*,  $\text{C}_{22}\text{H}_{32}\text{N}_2\text{PtCl}_6$ , crystallising in lustrous tablets and melting at  $216^\circ$ . *Methyl tripropylammoniumiodoacetate* crystallises in lustrous, rhombic leaflets or in large, yellowish prisms [ $a:b:c=0.9041:1:0.6975$ ], which melt at  $173-174^\circ$  and decompose at about  $200^\circ$ ; *tripropylammonium iodide* decomposes at about  $280^\circ$  and can be crystallised from dilute alkalis; *methyltripropylammonium iodide* crystallises in lustrous leaflets and melts at  $207-208^\circ$ .

*Methyl pyridiniumiodoacetate*, prepared from pyridine and methyl

iodoacetate, separates from water in colourless crystals, which decompose at 144—145°, and forms an iodine additive compound,  $C_8H_{10}O_2NI_2$ , which crystallises from alcohol and decomposes at 102—104°.

*Phenacylphenyldimethylammonium bromide* is deliquescent, crystallises from alcohol or ether, sinters at about 115°, and melts at 125—128°. *Phenacyl-p-tolylmethylethylammonium bromide* crystallises in colourless needles and melts at 116—117° without decomposition.

R. H. P.

**Aromatic Polycarbylamines.** By FELIX KAUFLEDER (*Monatsh.*, 1901, 22, 1073—1082).—Previous failures to obtain polycarbylamines have been due to the instability of these substances in boiling alcoholic potash. By using an excess of chloroform and a concentrated aqueous solution of potassium hydroxide containing 20—40 per cent. of alcohol, the author has obtained dicarbylamines from *p*- and *m*-phenylenediamine. *p*-Phenylenedicarbylamine forms white, triclinic needles and plates [ $a:b:c = 0.8489 : 0.9571 : 1$ ;  $\alpha = 87^\circ 42'$ ;  $\beta = 105^\circ 15'$ ;  $\gamma = 107^\circ 38'$ ] which darken on exposure to air and commence to blacken at 140°. A mol. weight determination showed that polymerisation had not taken place. With bromine dissolved in ether, the dicarbylamine forms *p*-phenylenedicarbylamine tetrabromide, which crystallises from ether in long, glistening, colourless needles melting at 137—138°. On exposure to light, the crystals become violet, the change of colour being accompanied by loss of bromine. On boiling the compound with absolute methyl alcohol, the bromine is entirely eliminated, and the tetrabromide also reacts with boiling aniline. Isomeric change of the dicarbylamine into terephthalonitrile commences at 160°, and takes place with explosive violence between 230° and 260°. The nitrile melts at 222—223° (corr.), and is hydrolysed by dilute hydrochloric acid to terephthalic acid. The dicarbylamine reacts energetically with acetyl chloride and with benzoyl chloride, is decomposed by boiling dilute acids and alkalis, and is instantly charred by concentrated sulphuric acid. It decolorises potassium permanganate in acid and alkaline solutions.

*m*-Phenylenedicarbylamine forms long, light yellow needles, which, when exposed to air, change into a dark brown, amorphous mass. The crystals blacken at 80° and melt at 95° with evolution of gas. The dicarbylamine decolorises potassium permanganate and bromine solutions. When heated, it is converted into isophthalonitrile melting at 154—155°, which on hydrolysis gives isophthalic acid melting at 310—320°.

The action of chloroform and potassium hydroxide on 2:4-diamino-1:3:5-trimethylbenzene yields needles which cannot be purified, but which, on heating, change into 2:4-dicyano-1:3:5-trimethylbenzene. With 2:4:6-triaminotoluene, the reaction gives a small quantity of a substance having the characteristic odour of the carbylamines. Triaminomesitylene yields a substance which blackens at 160°, and has the odour of a carbylamine. The analytical results agree with those required by 4:6-diisocyano-2-hydroxy-1:3:5-trimethylbenzene.

G. Y.



**Action of Alcoholic Potassium Hydroxide or Formaldehyde on Nitrosobenzene.** By EUGEN BAMBERGER (*Ber.*, 1902, 35, 732—738).—*N*-Formyl- $\beta$ -phenylhydroxylamine results from the action of potassium hydroxide dissolved in ethyl alcohol on nitrosobenzene; it crystallises from hot water or any of the ordinary mineral solvents in colourless plates or silky needles and melts at 70—71°. In aqueous ferric chloride solution, the formyl compound develops an intense reddish-violet coloration, which changes to greenish-brown on the addition of strong hydrochloric acid. The *copper* derivative,  $\text{Cu}(\text{O}\cdot\text{NPh}\cdot\text{CHO})_2$ , is insoluble in water, but crystallises from alcohol in light green, flattened needles; its decomposition point is ill-defined, lying between 225° and 230°.

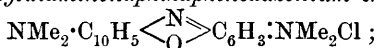
When the nitrosobenzene and potassium hydroxide are dissolved in methyl alcohol, the reaction leads to the formation of azoxybenzene, nitrobenzene, and *p*-aminophenol; *N*-formyl- $\beta$ -phenylhydroxylamine is not produced.

Formaldehyde and nitrosobenzene react in methyl alcohol solution, giving rise to azoxybenzene, *N*-formyl- $\beta$ -phenylhydroxylamine, aniline, and probably traces of formanilide and *p*-aminophenol. G. T. M.

**$\alpha$ -Naphthylamine Derivatives.** By V. FUSSGANGER (*Ber.*, 1902, 35, 976—984. Compare Friedländer and Welmans, *Abstr.*, 1889, 150).—When dimethyl- $\alpha$ -naphthylamine is heated with 90 per cent. sulphuric acid at 130°, a mixture of two monosulphonic acids is obtained, which may be separated by the aid of cold water, in which the 5-sulphonic acid is practically insoluble. The positions of the sulphonic acid groups were established by alkylating the various 1-naphthylaminesulphonic acids and comparing these products with the two acids obtained by sulphonating the alkylated base.

1-Dimethylaminonaphthalene-4-sulphonic acid,  $\text{NMe}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$ , obtained by the action of methyl iodide, methyl alcohol, and sodium hydroxide (1 mol.) on naphthionic acid at 100—110° for 6—8 hours, crystallises from hot water in well-developed, quadratic prisms containing  $1\text{H}_2\text{O}$ . With concentrated hydrochloric acid, it forms a soluble salt which is hydrolysed by water.

The dimethylamino-5-sulphonic acid also crystallises with  $1\text{H}_2\text{O}$  in quadratic prisms and closely resembles the 4-acid. Its solutions exhibit a green fluorescence, and when fused with potash, it yields 1-dimethylamino-5-hydroxynaphthalene in the form of hexagonal plates melting at 110° and identical with the compound described in the D.R.-P. No. 50142. With *p*-nitrosodimethylaniline, it yields a greenish-blue dye, probably tetramethyldiaminonaphthaphenoxazonium chloride,



it dissolves readily in water and is a strong base, is turned violet by concentrated sulphuric acid, and gives a pure indigo blue on cotton mordanted with tannic acid or tartar emetic. The similar dye obtained from nitrosodiethylaniline is somewhat greener in colour.

5-Dimethylamino- $\alpha$ -naphthol and *p*-nitroso-*m*-dimethylaminophenol yield a pure blue dye, which is turned yellowish-red by concentrated sulphuric acid. Nitrous acid reacts with 5-dimethylamino- $\alpha$ -naphthol

suspended in acetic acid, yielding 6-nitroso-1-dimethylamino-5-hydroxy-naphthalene (1-dimethylamino-5:6-naphthaquinoneoxime) in the form of yellow, pointed needles, and condenses with amines and aminophenols to form quinoneimide dyes.

1-Diethylaminonaphthalene-5-sulphonic acid crystallises with  $1\text{H}_2\text{O}$  in long, colourless needles and dissolves in concentrated hydrochloric acid, dilute alkalis, or alcohol.

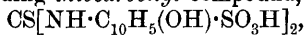
1-Methylaminonaphthalene-6-sulphonic acid, obtained by methylating  $\alpha$ -naphthylamine-6-sulphonic acid, forms a soluble sodium salt which crystallises with  $1\text{H}_2\text{O}$ .

1-Dimethylaminonaphthalene-7-sulphonic acid is readily soluble in water, and its sodium salt crystallises in colourless plates containing  $1\text{H}_2\text{O}$ .

1-Dimethylaminonaphthalene-8-sulphonic acid forms a soluble sodium salt containing  $1\text{H}_2\text{O}$ , and the free acid is readily soluble in both dilute acids or alkalis.

J. J. S.

**Naphthalenoid Carbamide and Thiocarbamide Sulphonic Acids containing free Hydroxyl Groups.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 123693).—When a mixture of 6-amino- $\alpha$ -naphthol-3-sulphonic acid and 7-amino- $\alpha$ -naphthol-3-sulphonic acid, dissolved in an aqueous solution of sodium carbonate, is treated with carbonyl chloride, carbonyl-8:5'-dihydroxydi- $\beta$ -naphthylamine-6:7'-disulphonic acid,  $\text{CO}[\text{NH}\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{SO}_3\text{H}]_2$ , is obtained as a soluble, grey powder which combines with diazonium salts but is not affected by nitrous acid. The corresponding thiocarbonyl compound,



produced by substituting thiocarbonyl chloride for its oxygen analogue in the preceding reaction, is a soluble, white powder. Carbonyl derivatives of other aminonaphtholsulphonic acids are also described (compare D.R.-P. 116200).

G. T. M.

**Preparation of Iodine Substitution Derivatives of Phenols.** By E. RICHARD (*J. Pharm. Chim.*, 1902, [vi], 15, 217—221).—Iodine substitution derivatives of phenols are readily prepared by the action of an aqueous solution of iodine on an aqueous solution of the phenol, containing either sodium hydrogen carbonate, disodium hydrogen phosphate, or sodium acetate. The hydriodic acid liberated by the action of the iodine on the phenol reacts with the added sodium salt with formation of sodium iodide. Sodium hydrogen carbonate can only be used in those cases in which substitution takes place without the application of heat. Several mono-, di-, and tri-iodophenols have been prepared by this method.

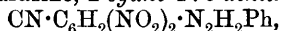
H. R. LE S.

**Iodophenols.** By P. BRENANS (*Compt. rend.*, 1902, 134, 357—360).—The tri-iodophenol obtained by the action of iodine on sodium phenoxide (Abstr., 1883, 1109) is the 2:4:6-derivative, and the di-iodophenol formed in the same way is the 2:6-derivative. The latter yields 3:5-di-iodo-*p*-hydroxybenzaldehyde when treated with chloroform and potassium hydroxide, and the 2:4:6-tri-iodide when

treated with iodine and mercuric oxide. The tri-iodophenyl allyl ether, prepared from this tri-iodophenol, melts at  $156^{\circ}$ . Derivatives of the di-iodophenol were prepared as follows: *di-iodoanisole*, in prismatic crystals melting at  $35^{\circ}$ ; *di-iodophenetole*, in prismatic crystals melting at  $41-42^{\circ}$ ; *di-iodophenyl allyl ether*, in tabular crystals melting at  $46^{\circ}$ ; *di-iodophenyl benzyl ether*, in prisms melting at  $74.5^{\circ}$ . When treated with fuming nitric acid, the di-iodophenol yields 4-nitro-2:6-iodophenol melting at  $156.5^{\circ}$ , and this yields a *methyl ether* in acicular crystals melting at  $133-134^{\circ}$ , and an *acetate* in similar crystals melting at  $194-195^{\circ}$ . The action of the nitric acid also yields a 6-nitro-2-iodophenol melting at  $110^{\circ}$ ; its *methyl ether* melts at  $60-61^{\circ}$ , and its *acetate* at  $96-97^{\circ}$ .

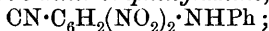
The action of nitric acid on *o*-iodophenol yields 2-iodo-6-nitrophenol melting at  $110^{\circ}$ , and 2-iodo-4-nitrophenol melting at  $86-87^{\circ}$ . The latter yields a *methyl ether* melting at  $97^{\circ}$ , and an *acetate* melting at  $68^{\circ}$  (compare Busch, *Ber.*, 1874, 7, 462). C. H. B.

**2-Cyano-4:6-dinitrophenol and some of its Derivatives.** By J. J. BLANKSMA (*Rec. Trav. Chim.*, 1901, 20, 411—421).—*o*-Ethoxybenzonitrile on nitration yields 3:5-dinitro-2-ethoxybenzonitrile, which crystallises in leaflets melting at  $72^{\circ}$ . Its properties are in every way similar to those of the ethyl ether of picric acid. With ammonia, the ethoxy-group is replaced by an amino-group, 2-amino-3:5-dinitrobenzonitrile,  $\text{CN}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{NH}_2$ , being produced; it forms yellow crystals melting at  $219^{\circ}$ , and does not react with carbon disulphide or benzaldehyde. With phenylhydrazine, 2-cyano-4:6-dinitrohydrazobenzene,



is obtained as red crystals decomposing at  $270-280^{\circ}$ ; with hydrazine, 2-cyano-4:6-dinitrophenylhydrazine is formed as red crystals decomposing at  $280^{\circ}$ , and with hydroxylamine, 2-cyano-4:6-dinitrophenylhydroxylamine, which forms yellow crystals melting at  $200^{\circ}$ . With alkali hydroxides, the ethyl ether is converted into 2-cyano-4:6-dinitrophenol, a substance closely resembling picric acid; it forms compounds with naphthalene (pale yellow needles, m. p.  $125-130^{\circ}$ ), with anthracene (ruby-red needles, m. p.  $164-165^{\circ}$ ), and yellow precipitates with alkaloids. The *strychnine* and *cinchonine* salts were analysed.

With phosphorus pentachloride, the phenol gives 1-chloro-2-cyano-4:6-dinitrobenzene, which forms yellow crystals melting at  $139^{\circ}$ , and with aniline yields 2-cyano-4:6-dinitrodiphenylamine,



the latter crystallises in yellow needles melting at  $183^{\circ}$ . With sodium sulphide, dicyanotetranitrophenyl sulphide is obtained as yellow crystals melting at  $238^{\circ}$ . K. J. P. O.

**Aromatic Derivatives of Sulphur.** By J. J. BLANKSMA (*Rec. Trav. Chim.*, 1901, 20, 399—410. Compare *Abstr.*, 1901, i, 264, and preceding abstract).—*o*-Nitrophenyl mercaptan,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SH}$ , prepared by the action of sodium sulphide on *o*-chloronitrobenzene, melts at  $45^{\circ}$ , and is oxidised by the air to 1:1'-dinitrodiphenyl disulphide (m. p.  $195^{\circ}$ ). 4-Chloro-2-nitrophenyl mercaptan,  $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{SH}$ , forms yellow crystals melting at  $122^{\circ}$ , and by iodine in alcoholic solution is readily converted into the *disulphide* melting at  $212^{\circ}$  (compare Beilstein and

Kurbatoff, Abstr., 1879, 230); 4-bromo-2-nitrophenyl mercaptan forms yellow crystals melting at  $110^{\circ}$ , and is oxidised by the air or by iodine into 4:4'-dibromo-2:2'-dinitrophenyl sulphide,  $\text{S}(\text{C}_6\text{H}_3\text{Br}\cdot\text{NO}_2)_2$ , melting at  $165^{\circ}$ . By nitric acid the latter is converted into the sulphoxide,  $\text{SO}(\text{C}_6\text{H}_3\text{Br}\cdot\text{NO}_2)_2$ , which melts at  $238^{\circ}$ .

*p*-Nitrophenyl mercaptan condenses with benzaldehyde in the presence of hydrochloric acid, yielding a mercaptal,  $\text{CHPh}(\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ , which forms yellow crystals melting at  $152^{\circ}$ .

*p*-Nitrophenyl methyl mercaptole,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SMe}$ , prepared from sodium *p*-nitrothiophenoxide and methyl iodide, melts at  $67^{\circ}$  and has a pleasant odour; the corresponding ethyl compound melts at  $40^{\circ}$ . 4-Chloro-2-nitrophenyl methyl mercaptole melts at  $128^{\circ}$ , and the corresponding bromo-derivative at  $126^{\circ}$ .

Sodium *o*-nitrothiophenoxide, and 1-bromo-2:4-dinitrobenzene yield a sulphide,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$ , as yellow crystals, melting at  $131^{\circ}$ ; similarly, an isomeric sulphide, melting at  $155^{\circ}$ , is obtained from sodium *p*-nitrothiophenoxide and 1-chloro-2:4-dinitrobenzene; from sodium 4-bromo-2-nitrothiophenoxide and 1-chloro-2:4-dinitrobenzene is formed 4-bromo-2:2':4'-trinitrophenyl sulphide melting at  $142^{\circ}$ . With nitric acid, the latter gives a sulphoxide melting at  $220^{\circ}$ . In a similar manner were prepared 4-chloro-2:2':4'-trinitrophenyl sulphide, (m. p.  $141^{\circ}$ ) and 4-bromo-2:2'-dinitrophenyl sulphide (m. p.  $131^{\circ}$ ). From the sodium derivative of thiofluorescein and 1-chloro-2:4-dinitrobenzene is obtained fluorescein 2:4-dinitrophenyl sulphide as yellow crystals melting at  $168^{\circ}$ .

In an analogous manner, chloro- (or bromo-) dinitrobenzene reacts with potassium xanthate, forming a dinitrophenyl ester of xanthic acid, which immediately decomposes into a dinitrophenyl mercaptan, carbon oxysulphide, and ethyl alcohol; the mercaptan then reacts with the excess of chlorodinitrobenzene, yielding tetranitrophenyl sulphide.

K. J. P. O.

[4-Nitro-2-aminophenol-6-sulphonic Acid.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 123611).—4-Nitro-2-aminophenol-6-sulphonic acid (Acid "III"), obtained by reducing 2:4-dinitrophenol-6-sulphonic acid with a solution of sodium sulphide and potassium hydroxide, and decomposing the resulting potassium salt with a mineral acid, crystallises in greyish-brown leaflets and decomposes at  $285^{\circ}$  with slight explosion. The mono- and di-potassium salts are crystalline, and the diazo-compound is very stable.

G. T. M.

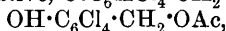
Action of Bromine and Chlorine on Phenols: Substitution Products:  $\psi$ -Bromides and  $\psi$ -Chlorides. By THEODOR ZINCKE (*Annalen*, 320, 145—178. Compare Abstr., 1899, i, 265).—A theoretical discussion bearing on the three succeeding abstracts and on work already published (compare Abstr., 1898, i, 70; 1899, i, 265, 616).

G. T. M.

Action of Bromine on Tetrachloro-*p*-cresol: Tetrachloro-*p*-cresol  $\psi$ -Bromide and its Transformation Products. By THEODOR ZINCKE and K. WIEDERHOLD (*Annalen*, 1902, 320, 179—198).—Tetrachloro-*p*-cresol  $\psi$ -bromide (tetrachloro-*p*-hydroxybenzyl bromide),

$\text{CO} \begin{smallmatrix} \text{CCl}:\text{CCl} \\ \text{CCl}:\text{CCl} \end{smallmatrix} \text{CH} \cdot \text{CH}_2\text{Br}$ , or  $\text{OH} \cdot \text{C}_6\text{Cl}_4 \cdot \text{CH}_2\text{Br}$ , prepared by heating tetrachloro-*p*-cresol and bromine in sealed tubes at  $100^\circ$ , crystallises in lustrous, white needles and melts at  $159\text{--}160^\circ$ ; it is reduced to tetrachloro-*p*-cresol by zinc and hydrochloric acid, whilst it dissolves in warm alkali hydroxide solution with loss of hydrogen bromide.

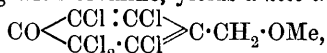
*Tetrachloro-p-hydroxybenzyl alcohol*,  $\text{OH} \cdot \text{C}_6\text{Cl}_4 \cdot \text{CH}_2 \cdot \text{OH}$ , results from the addition of water to an acetone solution of the preceding substance; it crystallises from benzene or acetone in lustrous needles decomposing at  $187\text{--}188^\circ$ , and dissolves in solutions of alkali carbonates and hydroxides; its *diacetyl* derivative,  $\text{OAc} \cdot \text{C}_6\text{Cl}_4 \cdot \text{CH}_2 \cdot \text{OAc}$ , crystallises from light petroleum in white needles melting at  $120^\circ$ . The  $\psi$ -bromide yields its *acetyl* derivative,  $\text{OAc} \cdot \text{C}_6\text{Cl}_4 \cdot \text{CH}_2\text{Br}$ , with acetic anhydride and the *monoacetyl* derivative,  $\text{O}:\text{C}_6\text{HCl}_4 \cdot \text{CH}_2 \cdot \text{OAc}$  or



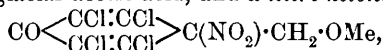
of the preceding alcohol with acetic acid and sodium acetate; the former of these crystallises in nacreous leaflets melting at  $128^\circ$ , the latter in white needles melting at  $170^\circ$ ; both these compounds yield the preceding diacetyl derivative when heated with acetic anhydride and sodium acetate.

The *nitro-ketone*,  $\text{O}:\text{C}_6\text{Cl}_4(\text{NO}_2) \cdot \text{CH}_2 \cdot \text{OH}$ , of tetrachloro-*p*-hydroxybenzyl alcohol, produced by adding nitric acid of sp. gr. 1.4 to a glacial acetic acid solution of the alcohol, is an unstable, white, amorphous substance decomposing at  $140^\circ$ ; it is converted into chloranil by hot nitric acid.

*Tetrachloro-p-hydroxybenzyl methyl ether*,  $\text{OH} \cdot \text{C}_6\text{Cl}_4 \cdot \text{CH}_2 \cdot \text{OMe}$ , obtained by boiling the  $\psi$ -bromide with methyl alcohol, separates from benzene in thick, white needles and melts at  $152\text{--}153^\circ$ ; it dissolves in solutions of the alkali hydroxides and carbonates, is reconverted into the  $\psi$ -bromide by heating with bromine, yields a *keto-chloride*,

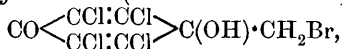


with chlorine in glacial acetic acid, and a *nitro-ketone*,



with nitric acid; the former derivative separates in monoclinic crystals melting at  $70\text{--}72^\circ$ , the latter is a yellowish-white precipitate decomposing at  $140^\circ$ .

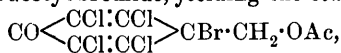
*Tetrabromohydroxytoluketone (tetrachlorobromotoluquinol)*,



results from the action of nitric acid of sp. gr. 1.4 and separates from benzene in stout, colourless needles melting at  $163\text{--}164^\circ$ ; its *acetyl* derivative,  $\text{O}:\text{C}_6\text{Cl}_4(\text{OAc}) \cdot \text{CH}_2\text{Br}$ , prepared with acetyl chloride, forms colourless leaflets and melts at  $143\text{--}144^\circ$ ; the hydroxy-ketone and its acetyl compound on reduction both yield tetrachloro-*p*-cresol.

The compound  $\text{CO} \begin{smallmatrix} \text{CCl}:\text{CCl} \\ \text{CCl}:\text{CCl} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{CH}_2 \end{smallmatrix}$ , obtained by treating the hydroxy-ketone with alcoholic sodium hydroxide, crystallises from benzene or alcohol in colourless needles melting at  $165\text{--}166^\circ$ . This

substance reacts with acetyl bromide, yielding the *compound*

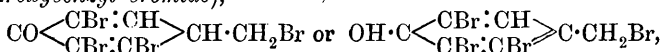


melting at 105°, which is isomeric with the acetyl derivative of the hydroxy-ketone; the corresponding *chloro*-derivative melts at 106—108°; these products both crystallise in lustrous, white leaflets.

G. T. M.

**Action of Bromine on *p*-Cresol: Substitution Products and  $\psi$ -Bromides of *p*-Cresol.** By THEODOR ZINCKE and K. WIEDERHOLD (*Annalen*, 1902, 320, 199—220).—*p*-Cresol, when dissolved in chloroform and treated with bromine, readily yields 3-bromo-*p*-cresol and 3:5-dibromo-*p*-cresol, the former being purified by distillation and the latter by crystallisation from alcohol. *Tribromo-p-cresol* results when the action is performed in the presence of powdered iron, the product being crystallised from glacial acetic acid or benzene; it separates in needles melting at 102°; its *acetyl* derivative forms thick, colourless needles and melts at 77°. *Tetrabromo-p-cresol*, obtained by heating the preceding compound with bromine and crystallising the product from glacial acetic acid, forms thick, lustrous needles melting at 196°, the sodium salt separates in quadratic leaflets and the *acetyl* derivative in lustrous, colourless needles melting at 156°.

[With FR. WAGNER in part.] *Tribromo-p-cresol*  $\psi$ -bromide (*tribromo-p-hydroxybenzyl bromide*),



prepared by heating tribromo-*p*-cresol with bromine in sealed tubes at 100°, crystallises from ether, benzene, or glacial acetic acid in colourless needles melting at 122°; it is insoluble in cold aqueous alkali hydroxides, but is decomposed by these reagents on warming. The substance is reduced to tribromo-*p*-cresol by zinc and hydrochloric acid and yields *tribromo-p-hydroxybenzyl alcohol*,  $\text{OH} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CH}_2 \cdot \text{OH}$ , when treated with water in acetone solution; the product crystallises from benzene in colourless needles melting at 138° and decomposing at 200°. It is soluble in sodium hydroxide solution and is reconverted into the  $\psi$ -bromide by hydrogen bromide dissolved in glacial acetic acid.

The *diacetyl* derivative,  $\text{OAc} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CH}_2 \cdot \text{OAc}$ , crystallises from benzene in colourless needles melting at 107°; the *monoacetyl* derivative,  $\text{O} \cdot \text{C}_6\text{H}_2\text{Br}_3 \cdot \text{CH}_2 \cdot \text{OAc}$  or  $\text{OH} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CH}_2 \cdot \text{OAc}$ , obtained by heating the  $\psi$ -bromide with acetic acid and sodium acetate, forms rhombic plates and melts at 123°. The  $\psi$ -bromide, when heated with acetic anhydride, yields its *acetyl* derivative,  $\text{OAc} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CH}_2\text{Br}$ , a substance forming needles melting at 116°. These two acetyl derivatives, when heated with glacial acetic acid and fused sodium acetate, both give rise to the preceding diacetyl compound.

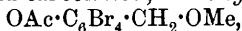
*Tribromo-p-hydroxybenzyl methyl ether*,  $\text{OH} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CH}_2 \cdot \text{OMe}$ , produced by heating the  $\psi$ -bromide with methyl alcohol, crystallises from benzene in colourless needles and melts at 72°; the *acetyl* compound melts at 60°.

*Tetrabromo-p-cresol*  $\psi$ -bromide (*tetrabromo-p-hydroxybenzyl bromide*),

$\text{O}:\text{C} \begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}:\text{CBr} \end{smallmatrix} \text{CH} \cdot \text{CH}_2\text{Br}$  or  $\text{OH} \cdot \text{C}_6\text{Br}_4 \cdot \text{CH}_2\text{Br}$ , formed by heating tribromo-*p*-cresol for 4 hours with excess of bromine in sealed tubes at  $100^\circ$ , crystallises from glacial acetic acid in lustrous needles and from benzene in white leaflets; it melts at  $182^\circ$ ; its acetyl derivative,  $\text{OAc} \cdot \text{C}_6\text{Br}_4 \cdot \text{CH}_2\text{Br}$ , obtained by the action of boiling acetic anhydride, separates from the ordinary organic solvents in nacreous leaflets melting at  $171$ — $172^\circ$ .

*Tetrabromo- $p$ -hydroxybenzyl alcohol*,  $\text{OH} \cdot \text{C}_6\text{Br}_4 \cdot \text{CH}_2 \cdot \text{OH}$ , produced by adding water to the acetone solution of the preceding  $\psi$ -bromide, crystallises from this solvent or from benzene in lustrous needles, sublimes above  $200^\circ$ , and decomposes at  $250^\circ$ ; it is soluble in solutions of the alkali hydroxides and carbonates, zinc and hydrochloric acid reduce it to tetrabromo-*p*-cresol, whilst hydrogen bromide in glacial acetic acid or methyl alcohol regenerates the  $\psi$ -bromide. The *diacetyl* derivative,  $\text{OAc} \cdot \text{C}_6\text{Br}_4 \cdot \text{CH}_2 \cdot \text{OAc}$ , forms white, silky needles and melts at  $154$ — $156^\circ$ .

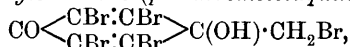
*Tetrabromo- $p$ -hydroxybenzyl methyl ether*,  $\text{OH} \cdot \text{C}_6\text{Br}_4 \cdot \text{CH}_2 \cdot \text{OMe}$ , results from the action of boiling methyl alcohol on the  $\psi$ -bromide; it crystallises in slender needles, melts at  $144^\circ$ , and dissolves in solutions of the alkali hydroxides and carbonates; its *acetyl* derivative,



forms white needles and melts at  $177$ — $178^\circ$ .

The *monoacetyl* derivative,  $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}:\text{CBr} \end{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{OAc}$  or  $\text{OH} \cdot \text{C}_6\text{Br}_4 \cdot \text{CH}_2 \cdot \text{OAc}$ , of tetrabromo-*p*-hydroxybenzyl alcohol, produced by heating the  $\psi$ -bromide with glacial acetic acid and sodium acetate, crystallises in needles and melts at  $159$ — $160^\circ$ ; it is converted into the diacetyl compound by acetic anhydride.

*Pentabromohydroxytoluketone (pentabromotoluquinol)*,

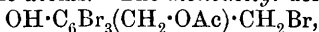


obtained by warming the tetrabromo- $\psi$ -bromide with nitric acid of sp. gr. 1.4, separates from the ordinary organic solvents in prismatic crystals or rhombohedra and melts at  $195^\circ$ ; it is reduced by zinc and hydrochloric acid to tetrabromo-*p*-cresol and yields a characteristic anilide; its *acetyl* derivative,  $\text{O}:\text{C}_6\text{Br}_4(\text{OAc}) \cdot \text{CH}_2\text{Br}$ , produced by means of acetyl chloride or bromide, crystallises in lustrous needles and melts at  $175$ — $176^\circ$ .

The compound  $\text{O}:\text{C}_6\text{Br}_4 \begin{smallmatrix} \text{O} \\ \text{CH}_2 \end{smallmatrix}$ , prepared by treating the preceding hydroxy-ketone with alcoholic sodium hydroxide solution, crystallises in needles from acetone and in leaflets from glacial acetic acid and decomposes at  $197$ — $198^\circ$ ; it is insoluble in aqueous solutions of the alkali hydroxides, but dissolves in the alcoholic alkaline solution; its anilide crystallises in lustrous, brown leaflets. G. T. M.

**Tribromo-4-hydroxy-*m*-xylene  $\psi$ -Dibromide.** By THEODOR ZINCKE and E. TRIPP (*Annalen*, 1902, 320, 220—231. Compare Auwers and Ziegler, *Abstr.*, 1897, i, 33).—Tribromo-4-hydroxy-*m*-xylene  $\psi$ -dibromide (pentabromo-4-hydroxy-*m*-xylene) is readily pre-

pared by heating tribromo-4-hydroxy-*m*-xylene and bromine in sealed tubes at 100°; it has a constitution represented either by  $\text{O}:\text{C}_6\text{HBr}_3(\text{CH}_2\text{Br})_2$  or  $\text{OH}\cdot\text{C}_6\text{Br}_3(\text{CH}_2\text{Br})_2$ , for it contains two readily exchangeable bromine atoms. The *monoacetyl* derivative,



obtained by the action of hot glacial acetic acid and silver acetate on the  $\psi$ -dibromide, crystallises in white, felted needles and melts at 148—152°; the diacetyl derivative,  $\text{OH}\cdot\text{C}_6\text{Br}_3(\text{CH}_2\cdot\text{OAc})_2$ , melts at 170° (Auwers gives 172°); the *triacetyl* compound,  $\text{OAc}\cdot\text{C}_6\text{Br}_3(\text{OAc})_2$ , forms rhombohedral crystals melting at 98—99°. The acetyl derivative,  $\text{OAc}\cdot\text{C}_6\text{Br}_3(\text{CH}_2\text{Br})_2$ , of the  $\psi$ -dibromide, obtained by the action of acetic anhydride, melts at 178—179°.

*Pentabromo-m-hydroxyxyloketone (pentabromo-m-xyloquinol),*



produced by treating the pentabromide with nitric acid of sp. gr. 1.4, crystallises in colourless prisms and melts at 182°; it is reduced to tribromo-4-hydroxy-*m*-xylene by zinc and hydrobromic acid; its *acetyl* derivative,  $\text{O}:\text{C}_6\text{Br}_3(\text{CH}_2\text{Br})_2\cdot\text{OAc}$ , forms needles melting at 158°.

The compound  $\text{O}:\text{C}_6\text{Br}_3(\text{CH}_2\text{Br})\text{C}(\text{O})\text{CH}_2$ , resulting from the action of sodium hydroxide on pentabromo-*m*-hydroxyxyloketone, crystallises from the ordinary organic solvents in pale yellow, silky needles; its *additive* product,  $\text{O}:\text{C}_6\text{Br}_4(\text{CH}_2\text{Br})\cdot\text{CH}_2\cdot\text{OAc}$ , with acetyl bromide, crystallises from glacial acetic acid in lustrous, white leaflets and melts at 142°.

G. T. M.

*s*-Trinitroxyleneol. By J. J. BLANKSMA (*Rec. Trav. Chim.*, 1901, 20, 422—424).—*s*-Trinitroxyleneol,  $\text{C}_6\text{Me}_2(\text{NO}_2)_3\cdot\text{OH}$ , is prepared by the action of fuming nitric acid on *s*-xylenol; it crystallises in colourless needles melting at 104°, and resembles picric acid very closely, but does not react with potassium cyanide.

K. J. P. O.

**Third Tribromide of  $\psi$ -Cumenol.** By O. ANSELMINO (*Ber.*, 1902, 35, 795—798. Compare Abstr., 1899, i, 34, and this vol., i, 214).—

*Dibromo-o-hydroxy- $\psi$ -cumyl bromide*,  $\text{CMe}\begin{smallmatrix} \text{CMe}=\text{CBr} \\ \text{CBr}\cdot\text{C}(\text{OH}) \end{smallmatrix}\text{C}\cdot\text{CH}_2\text{Br}$ , is

prepared by the action of bromine on bromo-*o*-hydroxy- $\psi$ -cumyl bromide; it crystallises in needles melting at 119.5°, and is insoluble in alkali hydroxides. When boiled with methyl alcohol, it is converted into the corresponding *methyl ether* of dibromo-*o*-hydroxy- $\psi$ -cumyl

alcohol,  $\text{CMe}\begin{smallmatrix} \text{CMe}=\text{CBr} \\ \text{CBr}\cdot\text{C}(\text{OH}) \end{smallmatrix}\text{C}\cdot\text{CH}_2\cdot\text{OMe}$ , which crystallises in leaf-

lets with a silvery lustre melting at 43°. When the bromide is treated with potassium iodide in acetic acid solution, *dibromo-o-hydroxy- $\psi$ -cumyl iodide* is formed, crystallising in yellow needles melting at 124°. *Dibromo-o-hydroxy- $\psi$ -cumyl acetate* is formed on treating an acetic acid solution of the bromide with zinc dust, and crystallises in lustrous prisms melting at 116°.

K. J. P. O.

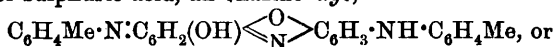
*m*-Hydroxyphenyl-*p*-tolylamine. By ROBERT GNEHM and LOUIS VEILLON (*J. pr. Chem.*, 1902, [ii], 65, 49—81).—*Acetyl-m-hydroxyphenyl-p-tolylamine*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NAc}\cdot\text{C}_6\text{H}_4\text{Me}$ , obtained by the action of



acetyl chloride or acetic anhydride on *m*-hydroxyphenyl-*p*-tolylamine, crystallises in quadratic tablets, melts at  $213^{\circ}$ , and dissolves sparingly in hot alcohol, ethyl acetate, or methyl alcohol, and more readily in glacial acetic acid; its *ethyl* ether, obtained by the action of ethyl iodide or ethyl sulphate on it, or by the action of acetyl chloride on *m*-ethoxyphenyl-*p*-tolylamine, crystallises in colourless, quadratic tablets and melts at  $61^{\circ}$ . The *barium* salt of the *disulphonic acid* of the acetyl derivative forms white needles containing  $1\text{H}_2\text{O}$ ; the *barium* salt of the *trisulphonic acid* could not be obtained in a crystalline state.

By the sulphonation of *m*-hydroxyphenyl-*p*-tolylamine under varying conditions, mono-, di-, and tri-sulphonic acids were obtained. The *monosulphonic acid* crystallises in microscopic, quadratic tablets, and is slightly soluble in hot water; its *potassium*, *sodium*, and *barium* salts are described. The *disulphonic acid* forms an indistinctly crystalline mass; its *potassium*, *sodium*, and *barium* (with  $1\text{H}_2\text{O}$ ) salts were prepared. The *barium* salt of the *trisulphonic acid* was obtained as a brownish powder. When the monosulphonic acid is heated with phthalic anhydride for 2 hours at  $170^{\circ}$ , the *disulphonic acid* of *s*-di-*p*-tolylrhodamine is produced; the same substance is obtained by the sulphonation of di-*p*-tolylrhodamine.

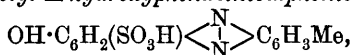
*m*-Hydroxyphenyl-*p*-tolylnitrosoamine melts at  $127^{\circ}$ . By the action of alcoholic hydrogen chloride at  $0^{\circ}$ , it is converted into the isomeric *nitroso-m*-hydroxyphenyl-*p*-tolylamine,  $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NO})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , which crystallises in dark red needles, melts at  $162\cdot2^{\circ}$ , and is easily soluble in alcohol, chloroform, or warm benzene; it is decomposed by sodium hydroxide with formation of *p*-toluidine and other products. When this compound is heated with a mixture of aniline and aniline hydrochloride, a *substituted azophenine*,  $\text{C}_{31}\text{H}_{26}\text{ON}_4$ , is produced, which crystallises from hot toluene in brown needles and melts at  $190^{\circ}$ . *p*-Amino-*m*-hydroxyphenyl-*p*-tolylamine,  $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , obtained by reducing the nitroso-compound with ammonium sulphide, crystallises in lustrous, silver-grey leaflets which, on exposure to air, rapidly turn dark blue; it melts at  $149^{\circ}$ , and dissolves readily in alcohol or ether and sparingly in benzene; its *hydrochloride* and *sulphate* form dark needles. *p*-Tolylamino-*m*-hydroxyphenyl- $\mu$ -cyanazomethine-*p*-nitrobenzene,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{N}\cdot\text{C}(\text{CN})\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , obtained by the action of *p*-nitrobenzyl cyanide on nitroso-*m*-hydroxyphenyl-*p*-tolylamine, crystallises in small, flat, red needles, melts at  $152^{\circ}$ , and is soluble in alcohol, ether, benzene, or toluene; the solution in benzene or toluene is strongly fluorescent. When nitroso-*m*-hydroxyphenyl-*p*-tolylamine is heated with *m*-hydroxyphenyl-*p*-tolylamine in presence of sulphuric acid, an oxazine dye,



$\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{C}_6\text{H}_2(\text{OH})\langle\text{N}\rangle\text{C}_6\text{H}_3\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$ , is produced, which crystallises in small, bluish-black needles, and is soluble in benzene, ether, alcohol, or glacial acetic acid; the *sulphate* is described.

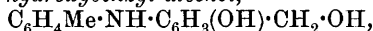
*m*-Hydroxyphenyl-*p*-tolylnitrosoaminesulphonic acid,  
 $\text{OH}\cdot\text{C}_6\text{H}_3(\text{SO}_3\text{H})\cdot\text{N}(\text{NO})\cdot\text{C}_6\text{H}_4\text{Me},$

obtained by the action of nitrous acid on *m*-hydroxyphenyl-*p*-tolyl-aminesulphonic acid, crystallises in lustrous, yellow, hexagonal plates, and is sparingly soluble in water or alcohol; the *sodium* and *potassium* salts form brown, rhombic crystals. Alcoholic hydrogen chloride converts it into *p*-tolyl-*m*-hydroxyphenazinesulphonic acid,



which forms a microcrystalline, violet-black powder, and is sparingly soluble in alcohol; its *barium* and *alkali* salts were prepared.

*p*-Tolylamino-*m*-hydroxybenzyl alcohol,



obtained by the action of formaldehyde (1 mol.) on *m*-hydroxyphenyl-*p*-tolylamine (1 mol.) in presence of hydrochloric acid (1 mol.), forms a yellow, amorphous powder and does not melt below 300°. If *m*-hydroxyphenyl-*p*-tolylamine (2 mols.) is heated with formaldehyde (1 mol.) and hydrochloric acid (2 mols.), *di-p*-tolyl-*di*aminodihydroxydiphenylmethane,  $\text{C}_{27}\text{H}_{26}\text{O}_2\text{N}_2$ , is obtained as a grey, amorphous powder, which melts at 118° and is readily soluble in alcohol, acetone, ether, or chloroform; the *hydrochloride* melts at 213°. This substance is also produced when *p*-tolylamino-*m*-hydroxybenzyl alcohol reacts with *m*-hydroxyphenyl-*p*-tolylamine in presence of hydrochloric acid.

By the action of bromine on *m*-hydroxyphenyl-*p*-tolylamine, the *pentabromo*-derivative is produced, which crystallises in rhombic tablets of a pearly lustre, melts at 203—204°, and is sparingly soluble in the usual organic solvents. The *pentanitro*-derivative crystallises in reddish-brown, hexagonal prisms, melts at 230°, and dissolves readily in acetone, chloroform, or glacial acetic acid; it explodes on percussion or on heating.

E. G.

**Guaiacolsulphonic Acid.** By HÄHLE (*J. pr. Chem.*, 1902, [ii], 65, 95—96).—By the action of concentrated sulphuric acid on guaiacol, Tiemann and Koppe (Abstr., 1882, 54) obtained a mixture of two sulphonic acids, one of which yielded a crystalline potassium salt, whilst the other furnished a potassium salt which could only be obtained in a syrupy condition. The author considers that the latter was due to impurities in the guaiacol.

Guaiacolsulphonic acid may be prepared by leaving a mixture of guaiacol and sulphuric acid monohydrate for several hours at the ordinary temperature, or by the action of sulphuric acid on guaiacol carbonate; the *sodium* salt crystallises in colourless leaflets. E. G.

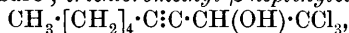
**Action of Nitric Acid on Trichloro- and Tribromo-veratrole.** By H. COUSIN (*Compt. rend.*, 1902, 134, 290—291. Compare Abstr., 1900, i, 179, 487, and 1901, i, 82).—Trichloroveratrole is not attacked by ordinary nitric acid, but by fuming nitric acid is converted into *trichloronitroveratrole*,  $\text{NO}_2 \cdot \text{C}_6\text{HCl}_3(\text{OMe})_2$ , which crystallises in white, silky needles melting at 94—96°.

*Tribromonitroveratrole*,  $\text{NO}_2 \cdot \text{C}_6\text{HBr}_3(\text{OMe})_2$ , prepared by the action of fuming nitric acid on tribromoveratrole, crystallises in lustrous, faintly yellow needles melting at 115—116°.

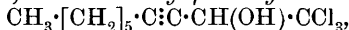
K. J. P. O.

**Condensation of Acetylenic Hydrocarbons with Aldehydes ; Synthesis of Secondary Alcohols with an Acetylenic Linking.** By CHARLES MOUREU and HENRI DESMOTS (*Compt. rend.*, 1902, 134, 355—357. Compare Abstr., 1901, i, 442).—When an aldehyde dissolved in ether is added to a molecular proportion of the sodium derivative of an acetylenic hydrocarbon suspended in ether, condensation readily takes place with production of a new class of secondary alcohols of the type  $\text{CR}:\text{C}\cdot\text{CHR}'\cdot\text{OH}$ . They form insoluble compounds with mercuric chloride in aqueous solution, and reduce ammoniacal silver nitrate with production of a mirror, but have no action on an alcoholic solution of silver nitrate.

The following alcohols were prepared in this way: *α-Phenyl-β-heptynyl alcohol*,  $\text{CH}_3\cdot[\text{CH}_2]_3\cdot\text{C}:\text{C}\cdot\text{CHPh}\cdot\text{OH}$ , which boils at 164—165° under 14 mm. pressure; *trichloromethyl-β-heptynylcarbinol*,



which boils at 141.5—142° under 12 mm. pressure; sp. gr. 1.2308 at 0°; *α-phenyl-β-octinyal alcohol*,  $\text{CH}_3\cdot[\text{CH}_2]_4\cdot\text{C}:\text{C}\cdot\text{CHPh}\cdot\text{OH}$ , which boils at 180—182° under 16 mm. pressure; sp. gr. 1.0031 at 0°; *α-furfuryl-β-octinyal alcohol*,  $\text{CH}_3\cdot[\text{CH}_2]_4\cdot\text{C}:\text{C}\cdot\text{CH}(\text{OH})\cdot\text{C}_4\text{OH}_3$ , which boils at 150—151° under 13 mm. pressure and melts at about -1°; sp. gr. 1.0176 at 0°; *trichloromethyl-β-octinyalcarbinol*,



which boils at 166° under 20 mm. pressure; sp. gr. 1.2018 at 0°; *furfuryl-β-octinyalcarbinol*,  $\text{CH}_3\cdot[\text{CH}_2]_5\cdot\text{C}:\text{C}\cdot\text{CH}(\text{OH})\cdot\text{C}_4\text{OH}_3$ , boiling at 163° under 13 mm. pressure; sp. gr. 1.004 at 0°; *phenylacetylenemethylcarbinol*,  $\text{CPh}:\text{C}\cdot\text{CHMe}\cdot\text{OH}$ , boiling at 148—149° under 29 mm. pressure; sp. gr. 1.0431 at 0°; *phenylacetylenetrichloromethylcarbinol*,  $\text{CPh}:\text{C}\cdot\text{CH}(\text{OH})\cdot\text{CCl}_3$ , boiling at 183—184° under 18 mm. pressure; sp. gr. 1.3809 at 0°; *phenylphenylacetylenecarbinol*,  $\text{CPh}:\text{C}\cdot\text{CHPh}\cdot\text{OH}$ , boiling at 220—222° under 20 mm. pressure; sp. gr. 1.116 at 0°; *furfurylphenylacetylenecarbinol*,  $\text{CPh}:\text{C}\cdot\text{CH}(\text{OH})\cdot\text{C}_4\text{OH}_3$ , boiling at 186—187° under 12 mm. pressure; sp. gr. 1.1601 at 0°.

C. H. B.

**Electrolytic Oxidation of *p*-Toluic Acid.** By HANS LABHARDT and R. ZSCHOCHE (*Zeit. Elektrochem.*, 1902, 8, 93—96).—*p*-Toluic acid, dissolved in excess of sodium hydroxide, is oxidised electrolytically to terephthalic acid or carbon dioxide. The best current efficiency is obtained when a platinum anode is used. At small current densities (0.04 ampere per sq. cm.), terephthalic acid is the main product; as the current density is increased, further complete oxidation to carbon dioxide takes place to an increasing extent.

T. E.

**Ethyl Phenylglycine-*o*-carboxylates.** CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 122687).—Ethyl phenylglycine-*o*-carboxylate,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  (m. p. 145—150°), is conveniently prepared by the action of ethyl chloroacetate on anthranilic acid in the presence of alcohol and sodium acetate or sodium carbonate. The isomeric *ester*,  $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , obtained by the action of chloroacetic acid on ethyl anthranilate, crystallises in needles melting at 167° (compare Abstr., 1900, i, 295).

G. T. M.

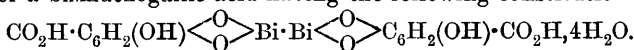
**Preparation of Indigotin.** HUGO ERDMANN (D.R.-P. 123695).—*Anthranilidoacetonitrile* ( $\omega$ -cyanomethylantranilic acid) prepared by condensing together anthranilic acid, hydrogen cyanide, and formaldehyde, melts at  $180^\circ$  and forms *methyl  $\omega$ -cyanomethylantranilate*,  $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CN}$ , on treatment with methyl sulphate dissolved in methyl alcohol in the presence of sodium carbonate. The ester melts at  $106.3^\circ$ , and when heated at  $160^\circ$  with acetic anhydride and anhydrous sodium acetate, it yields *methyl acetyl- $\omega$ -cyanomethylantranilate*, which crystallises in colourless needles and melts at  $83^\circ$ . The latter product, when mixed with naphthalene and heated at  $150$ – $170^\circ$  with potassium hydroxide, yields a product which, when extracted with water, oxidised by a current of air, and acidified with hydrochloric acid, gives rise to indigotin, the colouring matter being thus obtained in a crystalline form. *Ethyl  $\omega$ -cyanomethylantranilate*, prepared either by substituting ethyl sulphate for the methyl ester in the production of its lower homologue, or by treating silver  $\omega$ -cyanomethylantranilate with ethyl iodide, melts at  $89^\circ$ ; its *acetyl* derivative is oily, and may be employed in the preparation of indigotin.

G. T. M.

**Crystallised Bismuth Salicylate and Gallate.** By PAUL THIBAUT (*Ann. Chim. Phys.*, 1902, [vii], 25, 268–284. Compare Abstr., 1901, i, 593, 712).—The communication contains a full description of the preparation of crystallised bismuth salicylate and references to the older processes for obtaining the salt.

Bismuth gallate,  $\text{BiC}_7\text{H}_7\text{O}_7$ , prepared by adding crystallised gallic acid to hydrated bismuth oxide (compare Abstr., 1902, ii, 106) suspended in a small quantity of water, may be obtained in transparent, micaceous, yellow granules on allowing the reagents to remain in contact for 15 days.

The salt, which cannot be produced from the anhydrous bismuth oxide, dissolves in solutions of ammonia or the alkali hydroxides and carbonates with an appreciable rise of temperature; the product of the action of potassium hydroxide has the composition,  $\text{BiK}_2\text{C}_7\text{H}_7\text{O}_7\cdot 2\text{H}_2\text{O}$ , and a similar *sodium* compound has been obtained. This result confirms the belief that the bismuth compound is not a true gallate, but rather a bismuthogallic acid having the following constitution:



In this respect the compound resembles bismuth lactate and differs from the corresponding salicylate, which behaves towards alkali hydroxides as a true bismuth salt.

The gallic acid compound is not attacked by cold dilute sulphuric acid, but is decomposed and charred by the concentrated acid.

G. T. M.

**Aminosulphosalicylic Acids.** JOSEPH TURNER (D.R.-P. 123115).—The nitrosalicylic acids, when boiled with solutions of sodium hydrogen sulphite, yield amino-sulphonic acids.

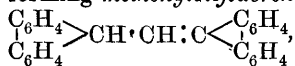
*o*-Aminosulphosalicylic acid,  $\text{NH}_2\cdot\text{C}_6\text{H}_2(\text{OH})(\text{CO}_2\text{H})\cdot\text{SO}_3\text{H}$ , a brownish-yellow powder, yields a soluble, greyish-white diazonium

compound, and develops a yellowish-brown coloration with chromic acid.

*p*-Aminosulphosalicylic acid and its diazonium compound are far less soluble than the corresponding ortho-derivatives; the free acid develops a reddish-brown coloration with chromic acid. G. T. M.

**Bimolecular Coumarone.** By JOHANNES BOES (*Chem. Centr.*, 1902, i, 355; from *Apoth.-Zeit.*, 1902, 17, 14. Compare Abstr., 1901, i, 31).—When the polymeride of coumarone ( $C_8H_6O$ )<sub>4</sub>, which melts at 107—108°, is distilled under 20 mm. pressure, the fraction boiling at 230—240° on redistillation yields, not only thin, oily portions, which are stable, and acid oils, but also 1·5 per cent. of bimolecular coumarone ( $C_8H_6O$ )<sub>2</sub>, which separates in crystals after the distillate has been kept for a long time. It melts at 99°, gives a carmine-red solution in sulphuric acid, and forms yellow nitro-derivatives, but is not attacked by hydrochloric acid or alkalis; a determination of the molecular weight gave 232. Attempts to convert the lower polymerides into the higher failed. Some clue to the mechanism of the process may possibly be more easily derived from experiments with coumarone or dicoumaryl. E. W. W.

**Ethyl Fluoreneoxalate.** By WILHELM WISLICENUS and ALFRED DENSCH (*Ber.*, 1902, 35, 759—765. Compare Abstr., 1900, i, 346).—The *phenylhydrazone* of fluoreneoxalic acid crystallises in slender, white needles and melts at 200—201°. The *oxime* of the ethyl ester crystallises from benzene and light petroleum and melts at 137—138°. Ethyl fluoreneoxalate, when treated with diazobenzene chloride, yields fluorenonephenylhydrazone, and when treated with methyl iodide and sodium methoxide, *ethyl methylfluoreneoxalate*,  $\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} > CMe \cdot CO \cdot CO_2Et$ , which boils at 210—215° under 12 mm. pressure, and when hydrolysed yields *methylfluorene*, which crystallises in prisms and melts at 46—47°. *Ethylfluorene*, obtained in an analogous manner, melts at 107—108° and boils at 165—166° under 13 mm. pressure. Ethyl fluoreneoxalate is easily benzoylated, yielding a *compound*,  $\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} > C : C(Obz) \cdot CO_2Et$ , which crystallises in long, yellow needles, melts at 141—142°, and, when treated with phenylhydrazine, yields benzoylphenylhydrazine and the phenylhydrazone of ethyl fluoreneoxalate. *p*-Nitrobenzoyl chloride, in the presence of sodium ethoxide, yields an analogous *compound*, which crystallises in yellow needles and melts at 188—189°. Ethyl formate, in the presence of sodium methoxide, slowly condenses with ethyl fluoreneoxalate, forming *methenylbisfluorene* (?),



which crystallises from toluene in slender, red needles and does not melt below 300°. R. H. P.

[Electrolytic Production of Benzaldehyde.] RICHARD NITHACK (D.R.-P. 123554).—An electrode composed of finely divided graphite

and benzoic acid is employed as the cathode of a cell, the anode being of lead or platinum. The solution in the cell consists of 20 per cent. sulphuric acid saturated with benzoic acid. On passing through the cell an electric current of 1.5 amperes per sq. decm. and 12—15 volts, benzaldehyde is produced, which forms an oily layer above the acid solution.

G. T. M.

**Condensation of Cinnamaldehyde with *iso*Butaldehyde.** By KARL MICHEL and KARL SPITZAUER (*Monatsh.*, 1901, 22, 1119—1139).

—When a mixture of cinnamaldehyde and *isobutaldehyde* is shaken with concentrated potassium carbonate solution, there is formed an aldol,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{CHO}$ , which is a thick oil having a pleasant, fruity odour; it reduces alkaline silver solutions and forms an additive product with bromine. When heated, the aldol decomposes, but if rapidly distilled at 190—200° under 20 mm. pressure, a small amount passes over unchanged. It forms an aldoxime,  $\text{C}_{13}\text{H}_{17}\text{O}_2\text{N}$ , which is a thick oil decomposing on distillation under reduced pressure. On reduction, the aldol yields the corresponding *glycol*,  $\text{C}_{13}\text{H}_{18}\text{O}_2$ , a slightly yellow oil which decomposes on distillation. The glycol combines with bromine, and yields a *diacetate*. Under the influence of potassium hydroxide, cinnamaldehyde and *isobutaldehyde* react rapidly with the formation of the aldol and a *hydroxy acid*,  $\text{C}_{13}\text{H}_{18}\text{O}_3$ , which on liberation from the potassium salt forms a *lactone*,  $\text{C}_{13}\text{H}_{16}\text{O}_2$ ; this distils, unchanged, at 343—345° under atmospheric pressure, melts at 89—90°, and does not form an additive product with bromine. The presence of excess of *isobutaldehyde* leads to the formation of octoglycol, whilst an increase in the proportion of potassium hydroxide increases the amount of the hydroxy-acid formed. The hydroxy-acid is also formed by the action of potassium hydroxide on the aldol. Oxidation of the acid by potassium permanganate in alkaline solution produces a dibasic acid,  $\text{C}_{13}\text{H}_{16}\text{O}_4$ , crystallising in short prisms which melt at 169°. When heated, the dibasic acid loses water at 210°, and is converted into an *anhydride* which distils at 243°, and, when crystallised from ether, forms four-sided prisms which melt at 111.5° and are converted into the acid on prolonged boiling with water. The constitution of the hydroxy-acid is probably  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$ , and that of the dibasic acid  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ . The latter, on distillation with lime, yields a substance which boils at 193—195°, and, on analysis, gives results agreeing with those required for the formula

$\text{CH}_2\text{Ph}\cdot\text{CH}\begin{matrix} \text{CMe}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{matrix}$ . The conversion of the aldol into the hydroxy-acid

remains without explanation, and the properties of the dibasic acid do not agree with those of an acid to which Bischoff ascribes the same constitution (*Abstr.*, 1891, 829).

G. Y.

**Condensation of Aromatic Aldehydes with Amines.** By OTTO DIMROTH and RUDOLF ZOEPPRITZ (*Ber.*, 1902, 35, 984—992).—

The first reaction between an aromatic aldehyde or ketone and an aromatic amine consists in the addition of the elements of the amine to the carbonyl group, and the second in the removal of a mol. of water. With a few exceptions (*Abstr.*, 1901, i, 378),

it has hitherto been found impossible to isolate the intermediate additive products. It is now shown that these products may readily be isolated in the form of their hydrochlorides when the condensation occurs in the presence of aqueous hydrochloric acid, since the salts are much more stable than the bases themselves. The same salts are also produced when the benzyldeneanilines are carefully treated with hydrochloric acid. It is found that the condensation between aldehydes and amines occurs much more readily and at lower temperatures when concentrated hydrochloric acid is present. The hydrochlorides thus produced vary considerably as regards their stability, those obtained from hydroxy-aldehydes being among the most stable. The corresponding free bases have been isolated, but in most cases show a great tendency to form the anhydrobenzyldene compounds.

*Benzaldehydeaniline hydrochloride*,  $\text{OH}\cdot\text{CHPh}\cdot\text{NHPh}\cdot\text{HCl}$ , decomposes before it can be completely dried, as does also the corresponding *p*-toluidine compound. *Benzaldehyde- $\beta$ -naphthylamine hydrochloride*,  $\text{OH}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7\cdot\text{HCl}$ , forms yellow crystals, melts at  $162\text{--}163^\circ$ , and is readily decomposed by water; treatment with sodium carbonate solution at  $0^\circ$  converts it into benzyldene- $\beta$ -naphthylamine.

*Benzaldehyde-p-nitroaniline hydrochloride*,  
 $\text{OH}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\cdot\text{HCl}$ ,  
 melts at about  $188^\circ$ , is insoluble in ether, but dissolves readily in alcohol and is decomposed by water at the ordinary temperature.

The corresponding base,  $\text{OH}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , melts at  $85\text{--}86^\circ$  (compare Miller and Plöchl, *Abstr.*, 1892, 1195; Hantzsch and Schwab, *ibid.*, 1901, i, 378).

*Salicylaldehydeaniline hydrochloride*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{NHPh}\cdot\text{HCl}$ , melts at  $93\text{--}94^\circ$ ; the base melts at  $48^\circ$  and readily loses water, yielding *o*-hydroxybenzyldeneaniline.

*p*-Hydroxybenzaldehydeaniline hydrochloride may be crystallised from warm 20 per cent. hydrochloric acid and forms yellow needles melting at  $215\text{--}217^\circ$ . The *platinichloride* crystallises in dark yellow needles melting at  $208\text{--}210^\circ$ . The base melts at  $170\text{--}175^\circ$  and gradually loses water, yielding *p*-hydroxybenzyldeneaniline.

Phenyliminobenzophenone melts at  $116^\circ$ , and not at  $112\text{--}113^\circ$  (Graebe, *Ber.*, 1899, 32, 1680) and dissolves in concentrated hydrochloric acid, yielding crystals of *benzophenoneaniline hydrochloride*,  $\text{OH}\cdot\text{CPh}_2\cdot\text{NHPh}\cdot\text{HCl}$ , melting at  $191\text{--}194^\circ$ ; it is immediately decomposed by water into benzophenone and aniline.

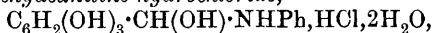
*2:4'-Diacetoxymbenzophenoneaniline hydrochloride*,  
 $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OH})(\text{NHPh})\cdot\text{C}_6\text{H}_4\cdot\text{OAc}\cdot\text{HCl}$ ,  
 is the compound previously described by Graebe as the corresponding anhydro-compound. J. J. S.

**Synthesis of Aromatic Hydroxyaldehydes.** By OTTO DIMROTH and RUDOLF ZOEPPRITZ (*Ber.*, 1902, 35, 993—997. Compare Gattermann, *Abstr.*, 1898, i, 581; 1899, i, 372).—Phosphorus oxychloride reacts with an ethereal solution containing molecular amounts of form-anilide and resorcinol, yielding *resorcinaldehydeaniline hydrochloride*,  $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}(\text{OH})\cdot\text{NHPh}\cdot\text{HCl}$ , in the form of small, yellowish needles.

It crystallises from dilute hydrochloric acid in rhombic prisms, melts and decomposes at  $140\text{--}141^\circ$ , and dissolves readily in alcohol, but is insoluble in benzene or ether. The *base*,  $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}(\text{OH})\cdot\text{NPh}$ , forms yellow crystals, melts at  $110^\circ$ , and in a vacuum over sulphuric acid loses water and yields the anhydro-compound, *dihydroxybenzylideneaniline*,  $\text{C}_6\text{H}_5(\text{OH})_2\cdot\text{CH}\cdot\text{NPh}$ . This melts at  $125\text{--}126^\circ$ , is readily soluble in alcohol or ether, and is converted into the original hydrochloride when warmed with 18 per cent. hydrochloric acid.

Resoreylaldehyde may be obtained by boiling the crude condensation product, containing both phosphoric acid and ether, with 3 per cent. sodium hydroxide solution.

*Pyrogallolaldehydeaniline hydrochloride*,



crystallises in yellow, prismatic needles with a bluish-violet lustre, melts at  $233\text{--}234^\circ$ , and is readily soluble in alcohol. The *platini-chloride* melts at  $224\text{--}226^\circ$ . The *base*,  $\text{C}_6\text{H}_2(\text{OH})_3\cdot\text{CH}(\text{OH})\cdot\text{NPh}$ , obtained by dissolving the hydrochloride in sodium acetate solution, crystallises in small prisms melting at  $179\text{--}180^\circ$ , and readily loses water, yielding 1:2:3-*trihydroxybenzylideneaniline* melting at  $194\text{--}195^\circ$ .

The original hydrochloride is readily decomposed when boiled with alkalis in a stream of hydrogen yielding pyrogallolaldehyde.

J. J. S.

**Nitro- and Amino-acetophenone (Hypnone).** By RUDOLF CAMPS (*Arch. Pharm.*, 1902, 240, 1—18).—Acetophenone was added gradually to nitric acid of sp. gr. 1.51 free from nitrous fumes, the temperature not being allowed to rise above  $-8^\circ$ . After a quarter-of-an-hour the solution was poured on to ice. Some crude *m*-nitroacetophenone separated and was filtered off; the mother liquor was neutralised at once with sodium carbonate and, finally, hydroxide, and extracted with ether, whereby crude *o*-nitroacetophenone was obtained. This extraction of the mother liquor is important, as one-third of the total yield (of 95 per cent.) was obtained in this way; previous workers have omitted this operation. The crude meta-compound was freed from admixed isomeride by continued suction; the crude ortho-compound by prolonged cooling at  $0^\circ$ , when some of the meta-isomeride crystallised out. Even after repeated fractionation, however, the oil still contained about 10 per cent. of the meta-compound.

Complete elimination of the meta-isomeride can best be effected after reduction; this was done with tin and hydrochloric acid, and the *o*-aminoacetophenone was distilled over with steam, the meta-compound, together with a little of the para-isomeride, remaining behind. *m*-Nitroacetophenone can be reduced in the same way; there is no need to precipitate the tin with hydrogen sulphide, for the bulk of the base can be precipitated as the stannichloride by adding excess of hydrochloric acid, and set free again by decomposing the precipitate with excess of sodium hydroxide, whilst the mother liquor can be concentrated, mixed with excess of sodium hydroxide, and extracted with ether. From 200 grams of acetophenone, there were obtained 145 of *m*- and 120 of *o*-nitroacetophenone; the latter was 90 per



cent. pure, and yielded readily 75—80 grams of *o*-aminoacetophenone.

A little *m*-nitrobenzoylformoxime,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH} \cdot \text{NOH}$ , is formed in the nitration, especially when this is carried out at 30—35°. It can be separated from the nitroacetophenones by means of its sparing solubility in ether. It melts at 152°, and yields *m*-nitrobenzoic and hydrocyanic acids when it is heated with aqueous alkalis. C. F. B.

**s-Dimethyldiaminodi-*o*-tolyl Ketone.** By ROBERT GNEHM and RALPH G. WRIGHT (*Ber.*, 1902, 35, 913—915).—*Dimethyldiaminoditolyl ketone*,  $\text{C}_{17}\text{H}_{20}\text{ON}_2$ , crystallises from acetone in pale yellow needles and melts at 80—81°. The *hydrochloride*,  $\text{C}_{17}\text{H}_{20}\text{ON}_2 \cdot 2\text{HCl}$ , crystallises from alcohol in flat, yellow prisms.

The *base* of auramine G (Gnehm and Schmid, American Patent No. 488430) forms yellow crystals and melts at 119—120°. The *picrate* crystallises from alcohol in glistening, orange-coloured needles and melts at 234°. The *sulphate* forms orange-coloured needles and melts at 182°. The *oxalate* is a yellow powder and melts at 210°.

The *hydrol*, prepared by reducing the ketone with sodium amalgam, crystallises from acetone in colourless needles, melts at 160—161°, and dissolves in acetic acid to a deep bluish-violet solution. With *p*-aminoazobenzene, it condenses to *benzeneazophenyl-leucauramine G*,  $\text{C}_{29}\text{H}_{31}\text{N}_5$ , which is precipitated from a solution in benzene by light petroleum in stout, orange-coloured tablets and melts at 170—170.5°. With benzeneazo- $\alpha$ -naphthylamine, *benzeneazo- $\alpha$ -naphthyl-leucauramine G*,  $\text{C}_{33}\text{H}_{33}\text{N}_5$ , is produced.

*Leucauramine G*, prepared by reducing auramine G with zinc dust and hydrochloric acid (Kern and Sandoz, D.R.-P. 64270) crystallises from benzene in yellow needles and melts at 207—208°.

By the action of hydrogen sulphide on a warm alcoholic solution of the hydrol, a colourless *thiohydrol* melting at 213—214° is produced. The *thio-ketone*,  $\text{C}_{17}\text{H}_{20}\text{N}_2\text{S}$ , from the auramine base and hydrogen sulphide, crystallises from alcohol in dull, blood-red crystals, melts at 176—177°, and forms two *hydrochlorides*,  $\text{C}_{17}\text{H}_{20}\text{N}_2\text{S} \cdot 2\text{HCl}$  and  $\text{C}_{17}\text{H}_{20}\text{N}_2\text{S} \cdot \text{HCl}$ , the former passing into the latter on exposure to the air. T. M. L.

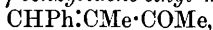
**Condensation of Methyl Ethyl Ketone with Benzaldehyde.** By CARL D. HARRIES and G. HANS MÜLLER (*Ber.*, 1902, 35, 966—971).—Benzaldehyde condenses with methyl ethyl ketone in the presence of sodium hydroxide, forming *benzylidenemethyl ethyl ketone*,  

$$\text{CHPh} \cdot \text{CH} \cdot \text{COEt},$$

which crystallises from light petroleum in lustrous laminae, melts at 38—39°, and boils at 142° under 12 mm. pressure. The *oxime* melts at 85—86° and the *phenylhydrazone* at 101°. When shaken with benzaldehyde, the ketone yields a white, crystalline *substance*, which melts at 65°, is probably a pyrone derivative, and forms an *oxime* melting at 195—196°. The *dibromo*-derivative crystallises in small needles and melts at 109—110°. When reduced, the ketone yields  *$\alpha$ -benzylmethyl ethyl ketone*, which is also obtained by the distillation of a mixture of calcium propionate and hydrocinnamate.  $\alpha$ -Benzylmethyl

ethyl ketone is a colourless, strongly refracting oil, which boils at 250—251° or at 128° under 17 mm. pressure, has  $n_D$  1.50882 at 20°, and forms an oily *oxime* and *phenylhydrazone*. A compound,  $C_{22}H_{26}O_2$ , which crystallises in white needles melting at 168—169°, is also obtained as a bye-product in the reduction of the benzylidene-ketone.

In the presence of hydrogen chloride, benzaldehyde and methyl ethyl ketone condense to form  $\gamma$ -benzylidene ethyl methyl ketone,



which crystallises from light petroleum in slender needles melting at 38° and boils at 127—130° under 12 mm. pressure. The *phenylhydrazone* crystallises from alcohol and melts at 105°. The *oxime* crystallises in large prisms melting at 103—104°, and the *dibromoderivative* melts at 61°. When the benzylidene-ketone is reduced, a 60 per cent. yield of  $\gamma$ -benzylethyl methyl ketone,  $CH_2Ph \cdot CH_2 \cdot CH_2 \cdot COMe$ , and an oily compound,  $C_{22}H_{26}O_2$ , which boils at 190—210° under 8 mm. pressure are obtained; the ketone is an oil which boils at 234° or at 110—115° under 13 mm. pressure, and has  $n_D$  1.50698 at 20°.

[Several of these compounds have been described by E. Levinstein (*Inaug. Diss. Berlin*)].

R. H. P.

**Monohydroxybenzylidenebromoidanones.** By K. MINIAT (*Bull. Soc. Chim.*, 1902, [iii], 27, 77—79).—The author has prepared a number of these compounds by the action of the hydroxybenzaldehydes on bromoidanone in presence of sodium hydroxide. *o*-Hydroxybenzylidene-2-bromoidanone is a pale red, crystalline substance which dissolves in hot dilute sodium hydroxide. Concentrated sulphuric acid colours the crystals red and yields an orange-coloured solution. The sodium salt crystallises in bright yellow needles which char at 220°. *2*-Bromo-*o*-acetoxyindanone, obtained by boiling the *o*-hydroxybenzylidenebromoidanone with acetic anhydride and fused sodium acetate, crystallises from alcohol in colourless needles which melt at 142°. *m*-Hydroxybenzylidene-2-bromoidanone crystallises from alcohol in long, shining needles which melt at 239°; concentrated sulphuric acid colours the crystals orange and yields a yellow solution. *m*-Acetoxybenzylidene-2-bromoidanone is slightly soluble in alcohol and crystallises in colourless leaflets melting at 173—174°. *p*-Hydroxybenzylidene-2-bromoidanone is formed with greater difficulty than its two isomerides; it is best obtained by heating the alcoholic solution of *p*-hydroxybenzaldehyde and bromoidanone with fuming hydrochloric acid for a short time in a reflux apparatus. It crystallises in small, yellow needles which melt at 252°. Sulphuric acid colours the crystals red and yields a yellow solution. The *acetoxy*-derivative crystallises from glacial acetic acid in colourless needles melting at 226—227°. The author has also prepared compounds by the action of furfuraldehyde, cuminaldehyde, and cinnamaldehyde on bromoidanone.

A. F.

**Disulphones. IX. Derivatives of Unsaturated Ketones containing Sulphur.** By THEODOR POSNER (*Ber.*, 1902, 35, 799—816. Compare Abstr., 1900, i, 5, 16; 1901, i, 14, 88, 474, 703).—The action of mercaptans on unsaturated ketones, which have one

or two ethylene linkings in the  $\beta$ -position to the carbonyl group, has been investigated.

Benzylideneacetone and benzyl mercaptan, when treated with hydrogen chloride in acetic acid solution, yield  $\beta\beta\gamma$ -trithiobenzyl- $\delta$ -phenylbutane,  $C_7H_7 \cdot S \cdot CHPh \cdot CH_2 \cdot CMe(SC_7H_7)_2$ , which forms a viscous, pale yellow oil. On oxidation, with aqueous potassium permanganate, of a solution in carbon tetrachloride,  $\beta\beta\gamma$ -tribenzylsulphone- $\delta$ -phenylbutane,  $C_7H_7 \cdot SO_2 \cdot CHPh \cdot CH_2 \cdot CMe(SO_2 \cdot C_7H_7)_2$ , is obtained as microscopic crystals melting at  $112-113^\circ$ .

$\beta\beta\gamma$ -Trithioamyl- $\delta$ -phenylbutane,  $C_5H_{11} \cdot S \cdot CHPh \cdot CH_2 \cdot CMe(S \cdot C_5H_{11})_2$ , prepared in a similar manner from amyl mercaptan and benzylideneacetone, is a mobile, pale yellow oil, and, on oxidation, does not yield a single sulphone.

Phenyl mercaptan and benzylideneacetone gave a mixture of mono- and tri-thiophenyl derivatives, which was oxidised to the sulphones. The latter were separated by crystallisation from water.

$\beta$ -Phenylsulphone- $\beta$ -phenylethyl methyl ketone,  
 $SO_2Ph \cdot CHPh \cdot CH_2 \cdot COMe$ ,

crystallises in needles, soluble in water and melting at  $115^\circ$ ;  $\beta\beta\gamma$ -triphenylsulphone- $\delta$ -phenylbutane,  $SO_2Ph \cdot CHPh \cdot CH_2 \cdot CMe(SO_2Ph)_2$ , the insoluble sulphone, crystallises in short needles melting at  $168^\circ$ .

Mesityl oxide and benzyl mercaptan do not yield a single substance. Amyl mercaptan and mesityl oxide give a mixture of mono- and tri-thio-derivatives, from which, on oxidation, one sulphone,  $\beta$ -amylsulphoneisobutyl methyl ketone,  $C_5H_{11} \cdot SO_2 \cdot CMe_2 \cdot CH_2 \cdot COMe$ , can be obtained in rhombic crystals melting at  $71^\circ$ .

Benzylideneacetophenone and benzyl mercaptan yield a mixture, from which, by oxidation, two sulphones can be obtained; these are separated by recrystallisation from alcohol.  $\beta$ -Benzylsulphone- $\beta$ -phenylethyl phenyl ketone,  $C_7H_7 \cdot SO_2 \cdot CHPh \cdot CH_2 \cdot COPh$ , melts at  $147-148^\circ$ ;  $\alpha\alpha\gamma$ -tribenzylsulphone- $\alpha\gamma$ -diphenylpropane,

$C_7H_7 \cdot SO_2 \cdot CHPh \cdot CH \cdot CPh(SO_2 \cdot C_7H_7)$

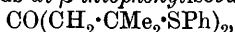
crystallises in lustrous needles melting at  $217^\circ$ .

Benzylideneacetophenone and amyl mercaptan give a mixture, on oxidation of which a sulphone,  $\beta$ -amylsulphone- $\beta$ -phenylethyl phenyl ketone,  $C_5H_{11} \cdot SO_2 \cdot CHPh \cdot CH \cdot COPh$ , is obtained melting at  $142-143^\circ$ . With phenyl mercaptan and the same ketone,  $\alpha$ -thiophenyl- $\beta$ -phenylethyl phenyl ketone,  $CH_2Ph \cdot CH(SPh) \cdot COPh$ , is formed, crystallising in needles melting at  $121^\circ$ ; on oxidation, it yields the corresponding sulphone melting at  $160-161^\circ$ . Dypnone and benzyl mercaptan yield a mixture of mercaptols; on oxidation,  $\beta$ -benzylsulphone- $\beta$ -methyl- $\beta$ -phenylethyl phenyl ketone,  $C_7H_7 \cdot SO_2 \cdot CMePh \cdot CH_2 \cdot COPh$ , is produced as a white, crystalline powder melting at  $137-138^\circ$ . From amyl mercaptan and dypnone is obtained an oily product yielding, on oxidation,  $\beta$ -amylsulpho- $\beta$ -methyl- $\beta$ -phenylethyl phenyl ketone,  $C_5H_{11} \cdot SO_2 \cdot CMePh \cdot CH_2 \cdot COPh$ , which crystallises in needles melting at  $143-144^\circ$ . From dypnone and phenyl mercaptan is formed  $\beta$ -thiophenyl- $\beta$ -methyl- $\beta$ -phenylethyl phenyl ketone,  $SPh \cdot CMePh \cdot CH_2 \cdot COMe$ , as a viscous, dark-yellow oil, which, on oxidation, gives a crystalline powder,  $\beta$ -phenylsulphone- $\beta$ -

*methyl-β-phenylethyl phenyl ketone*,  $\text{SO}_2\text{Ph}\cdot\text{CMePh}\cdot\text{CH}_2\cdot\text{COPh}$ , melting at  $100^\circ$ .

The substance previously described (Abstr., 1901, i, 474) as dibenzylideneacetonedisulphone (m. p.  $140\text{--}142^\circ$ ) is now shown to be *dibenzylacetonedithiethylsulphone*,  $\text{CO}(\text{CH}_2\cdot\text{CHPh}\cdot\text{SO}_2\text{Et})_2$ . Benzyl mercaptan and dibenzylideneacetone give a mixture of thio-derivatives, from the products of oxidation of which can be isolated *dibenzylacetonedibenzylsulphone*,  $\text{CO}(\text{CH}_2\cdot\text{CHPh}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7)_2$ , crystallising in needles melting at  $185^\circ$ . Amyl mercaptan and dibenzylideneacetone give *aryle-tetrathioamyl-α-diphenylpentane* as an oil; on oxidation, *dibenzylacetonediamylsulphone*,  $\text{CO}(\text{CH}_2\cdot\text{CHPh}\cdot\text{SO}_2\cdot\text{C}_5\text{H}_{11})_2$ , is obtained in small needles melting at  $155^\circ$ . Phenyl mercaptan and dibenzylideneacetone yield *dibenzylacetonedithiolphenyl*,  $\text{CO}(\text{CH}_2\cdot\text{CHPh}\cdot\text{SPh})_2$ , crystallising in needles melting at  $139\text{--}140^\circ$ , which is oxidised to the corresponding *sulphone*, crystallising in needles melting at  $166^\circ$ .

The substance previously described as phoronedisulphone (m. p.  $101^\circ$ , *loc. cit.*) is now shown to be *di-β-ethylsulphoneisobutyl ketone*,  $\text{CO}(\text{CH}_2\cdot\text{CMe}_2\cdot\text{SO}_2\text{Et})_2$ . Phorone and benzyl mercaptan yield *di-β-thiobenzylisobutyl ketone*,  $\text{CO}(\text{CH}_2\cdot\text{CMe}_2\cdot\text{SC}_7\text{H}_7)_2$ , as a pale yellow, mobile oil; this, on oxidation, is converted into the corresponding *disulphone*, which melts at  $171\text{--}172^\circ$ . With amyl mercaptan, phorone gives *di-β-thioamylisobutyl ketone*,  $\text{CO}(\text{CH}_2\cdot\text{CMe}_2\cdot\text{SC}_5\text{H}_{11})_2$ , as a pale yellow, mobile oil; the *disulphone* melts at  $127\text{--}128^\circ$ . With phenyl mercaptan, phorone yields *di-β-thiophenylisobutyl ketone*,



a mobile, yellow oil; the *disulphone* forms lustrous leaflets melting at  $160^\circ$ .

K. J. P. O.

**Preparation of Deoxybenzoin.** By HANS STOBBE (*Ber.*, 1902, 35, 911—912).—A solution of benzoin in 90 per cent. alcohol is reduced by adding purified zinc and passing in hydrogen chloride. The solution is poured into water, heated for some hours, and the crude deoxybenzoin carefully dried and then distilled. The yield by this method is from 60 to 75 per cent. of the theoretical quantity.

T. M. L.

**Hydroxylamino- and Nitroso-anthraquinone.** I. By LEONHARD WACKER (*Ber.*, 1902, 35, 666—669).—1-Hydroxylaminoanthraquinone-2-sulphonic acid is formed when 1:2-nitroanthraquinone-sulphonic acid is reduced with dextrose and sodium hydroxide; the reddish-brown sodium salt,  $\text{C}_{14}\text{H}_8\text{O}_6\text{NSNa}$ , was isolated and analysed. In presence of strong sulphuric acid at  $70\text{--}80^\circ$ , the hydroxylamino-compound undergoes isomeric change and 1-amino-4-hydroxyanthraquinone-2-sulphonic acid is formed; the sulphate is yellow, but the salts are bluish-violet in alkaline solution and dye wool violet. 1-Nitrosoanthraquinone-2-sulphonic acid is formed on oxidising the hydroxylamino-compound with potassium ferricyanide; the sodium salt,  $\text{C}_{14}\text{H}_6\text{O}_6\text{NSNa}$ , forms minute, yellow, glistening flakes, and is only sparingly soluble in water.

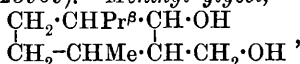
T. M. L.

**Derivatives of  $\alpha$ -Aminoalizarin.** By GUSTAV SCHULTZ and J. ERBER (*Ber.*, 1902, **35**, 906—908. Compare Roemer, *Abstr.*, 1885, 1068).—Two isomeric compounds result from the action of acetic anhydride on  $\alpha$ -aminoalizarin. When the base is mixed with sodium acetate and heated on a water-bath with acetic anhydride, a *diacetyl- $\alpha$ -aminoalizarin*,  $C_{18}H_{13}O_6N$ , is formed, which melts at  $205^\circ$  and crystallises unchanged from alcohol. When this compound, or the original base, is boiled with acetic anhydride, an *isomeride* is produced which forms reddish-brown flakes, melts at  $245^\circ$ , crystallises well from toluene, sublimates without decomposition, is hydrolysed by cold sodium hydroxide or by hot sodium carbonate, and when boiled with alcohol is converted into the isomeride melting at  $205^\circ$ .

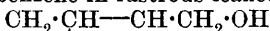
*Benzoyl- $\alpha$ -aminoalizarin*,  $C_{21}H_{13}O_5N$ , prepared by the action of benzoyl chloride on a solution of the base in boiling nitrobenzene, forms reddish-brown needles, is insoluble in ordinary solvents, but crystallises from nitrobenzene and sublimates with partial decomposition in brilliant red needles. *Dibenzoyl- $\alpha$ -aminoalizarin*,  $C_{28}H_{17}O_6N$ , separates from the mother liquors of the preceding compound in minute, brown needles, melts at  $255^\circ$ , and dissolves in chloroform, toluene, or nitrobenzene. *Dibenzoyl- $\beta$ -alizarin* can be readily prepared by a similar method; it forms yellow, glistening flakes, melts at  $252^\circ$ , is highly pyroelectric, and crystallises well from chloroform or toluene.

T. M. L.

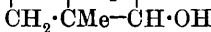
**Cyclic Dihydric Alcohols.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.P. 123909).—*Menthyl glycol*,



produced by reducing hydroxymethylenementhone with sodium and hot ethyl or amyl alcohol, is an oil which solidifies on cooling, and consists of a mixture of two stereoisomerides. *cis*-Menthyl glycol passes into solution on extracting the preceding substance with ether and crystallises from light petroleum in lustrous prisms melting at  $76$ — $78^\circ$  and boiling at  $164$ — $167^\circ$  under 16 mm. pressure. *trans*-Menthyl glycol crystallises from benzene in lustrous leaflets and melts at  $103$ — $104^\circ$ .



*Camphyl glycol*,  $\begin{array}{c} | \\ \text{CMe}_2 \\ | \end{array}$ , prepared from hydroxy-



methylenecamphor, is a mixture of two isomerides, the *trans*-modification forming lustrous leaflets melting at  $117$ — $118^\circ$ ; the *cis*-compound, however, was not obtained pure. The crude glycol boils at  $174$ — $176^\circ$  under 20 mm. pressure.

Hydroxymethylenedihydroisophorone yields the *cis*- and *trans*-*dihydroisophoryl glycols* the former crystallising in colourless leaflets melting at  $103^\circ$ , the latter forming a crystalline mass boiling at  $170^\circ$  under 17 mm. pressure.

G. T. M.

**Migration of the Methyl Group in the Molecule of Camphor.** By EDMOND E. BLAISE and G. BLANC (*Bull. Soc. Chim.*, 1902, [iii], **27**, 71—76).—The authors claim to have proved that the  $\alpha$ - and  $\beta$ -derivatives of camphor are not stereoisomeric.

*Dihydro- $\alpha$ -aminocampholene*,  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH} \begin{smallmatrix} \text{CMe}_2 \cdot \text{CHMe} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix}$ , is a colourless compound and has a more disagreeable odour than the  $\beta$ -derivative; it boils at  $190^\circ$ , has a specific rotation  $32.48^\circ$ , and a sp. gr. 0.8655 at  $15^\circ/15^\circ$ . The *picrate* crystallises from dilute alcohol in large, yellow laminae which melt and decompose at  $227^\circ$ . The *oxamide* forms long, silky needles melting at  $147$ – $148^\circ$ . The *platini-chloride* is very slightly soluble in water or alcohol, and when heated decomposes without melting. The *carbamide*,  $\text{C}_9\text{H}_{17} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , forms slender needles very slightly soluble in cold benzene, and melts at  $107$ – $108^\circ$ . In the preparation of the base, there is also formed the *ureide*,  $\text{C}_8\text{H}_{15} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C}_8\text{H}_{15}$ . When the carbamide is heated, dihydro- $\alpha$ -campholenonitrile is formed, and by hydration with acids or alkalis, dihydro- $\alpha$ -campholenic acid.

By the bromination of  $\alpha$ -dihydrocampholenic acid and subsequent esterification, *ethyl bromo- $\alpha$ -dihydrocampholenate*,  $\text{C}_8\text{H}_{15} \cdot \text{CHBr} \cdot \text{CO}_2\text{Et}$ , was obtained; it boils at  $135$ – $140^\circ$  under 12 mm. pressure. The *unsaturated acid*,  $\text{C}_8\text{H}_{14} \cdot \text{CH} \cdot \text{CO}_2\text{H}$ , obtained by the hydrolysis of the ester with alcoholic potash, readily crystallises from dilute alcohol or acetic acid in leaflets, melts at  $70^\circ$ , boils at  $155^\circ$  under 12 mm. pressure, is soluble in all organic solvents, absorbs bromine, and instantaneously decolorises alkaline permanganate. Adopting the  $\alpha$ -constitution given by Mahla and Tiemann for dihydrocampholenic acid (compare Abstr., 1900, i, 507), the ketone formed by the oxidation must have the constitution  $\text{CMe}_2 \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \\ \text{CO} - \text{CH}_2 \end{smallmatrix}$  (4:5:5-trimethylcyclopentanone), and ought therefore to be different from the 2:3:3-trimethylcyclopentanone of Noyes (compare Abstr., 1900, i, 202). This the authors find to be the case. 4:5:5-Trimethylcyclopentanone is a colourless liquid with an odour both of camphor and of mint; it boils at  $164$ – $165^\circ$ , and is insoluble in water. The *oxime* forms pearly scales, soluble in alcohol and in light petroleum, and melts at  $107$ – $108^\circ$ . The *semicarbazone* forms small crystals insoluble in water, and very slightly soluble in cold, but more so in hot, alcohol, and melts at  $188^\circ$  without decomposition. The *benzylidene* derivative,  $\text{C}_8\text{H}_{12}\text{O} \cdot \text{CHPh}$ , readily obtained by condensation in alkaline solution, crystallises in prisms which melt at  $34^\circ$  and are soluble in all organic solvents. A. F.

**Action of Arsenic Acid on Pinene.** By PAUL GENVRESSE (*Compt. rend.*, 1902, 134, 360–362).—When pinene is distilled with about one-fortieth of its weight of crystallised arsenic acid, small quantities of terpinene, cymene, and terpineol are produced, but the chief product is a liquid identical with the original pinene in chemical and physical properties, except that its odour is somewhat different and its optical activity less, being only  $-26^\circ 16'$  as compared with  $-40^\circ 51'$  for the original pinene. If, however, the arsenic acid amounts to a quarter of the weight of the pinene, the greater part of the latter is readily converted into terpinene, together with some terpineol and a little cymene. This terpinene has a rotatory power of  $-10^\circ 21'$  to  $-10^\circ 47'$  in a 20 cm. tube. Limonene, when treated in the same way, is also converted into terpinene. C. H. B.

**Algerian Oil of Rue.** By HUGO VON SODEN and KARL HENLE (*Chem. Centr.*, 1902, i, 256; from *Pharm. Zeit.*, 1901, 46, 1026—1027. Compare Abstr., 1901, i, 396).—The methyl heptyl ketone contained in Algerian oil of rue is the normal ketone, since, on oxidation, it yields normal octoic acid (caprylic acid), and by the action of phosphorus trichloride and ammonia it forms normal octamide (caprylamide); methyl heptyl ketoxime is also converted into normal heptylamine when treated with hot sulphuric acid by the Beckmann-Wallach method. The crude methyl heptyl ketoxime can be purified by distillation under reduced pressure, and then forms a clear liquid which boils at 108—109° under 6 mm. pressure, has a sp. gr. 0.882 at 20°, and solidifies at +14°. Normal heptylamine boils at 153—156°; the picrate crystallises from a mixture of ether and light petroleum in yellow needles, and melts at 118.5—119.5°. The Algerian oil, like the ordinary oil, is slightly fluorescent; it contains 90 per cent. of admixed methyl heptyl ketone and methyl nonyl ketone, the amount of the former being twice as great as that of the latter, and to this larger proportion of methyl heptyl ketone its peculiar odour is mainly due.

The esters contained in the oil and boiling at about 200—210°, appear to consist, for the most part, of the acetates of the secondary alcohols corresponding with the ketones. E. W. W.

**Essence of Ylang-ylang.** By GEORGES DARZENS (*Bull. Soc. Chim.*, 1902, [iii], 27, 83—85. Compare Abstr., 1895, i, 243, 294).—From the result of hydrolysis with aqueous potassium hydroxide, the author concludes that this essence probably contains methyl alcohol. He has also detected the presence of *p*-cresol, and confirmed the occurrence of benzoic and acetic acids already found by Reychler.

A. F.

**Colophony.** By WILHELM FAHRION (*Zeit. angew. Chem.*, 1902, 15, 83—84. Compare this vol., i, 165).—Polemical. A reply to Dietrich and a *résumé* of Schkateloff's work (Abstr., 1889, 406). J. J. S.

**Chlorophyll. VIII. Changes Undergone by Chlorophyll in passing through the Bodies of Animals.** By EDWARD SCHUNCK (*Proc. Roy. Soc.*, 1902, 69, 307—312).—Whilst the faeces of cows and sheep which have been fed exclusively on green vegetable food are found not to contain chlorophyll, certain derivatives of chlorophyll have been isolated therefrom. One of these appears to be phylloxanthin, and another, resembling phyllocyanin, is named by the author *scatocyanin*. The latter may be obtained by the extraction of dried cow dung with cold chloroform, and slow evaporation of the filtered solution, in the form of purplish-blue crystals with a brilliant metallic lustre. The substance is soluble in chloroform, boiling glacial acetic acid (fine crimson solution), concentrated sulphuric acid (grass-green to purplish-blue solution), boiling aniline (dull red solution), and alcoholic potash (yellow solution), but almost insoluble in boiling alcohol, ether, carbon disulphide, benzene, or aqueous potassium hydroxide. The absorption spectrum of the chloroform solution is nearly the same as that given

by phyllocyanin; the absorption spectra of the glacial acetic and sulphuric acid solutions are also described.

J. C. P.

**Hydrazides and Azoimides of Organic Acids. XXVI. Hydrazide [and Azoimide] of Pyromucic Acid.** By THEODOR CURTIUS and ROBERT LEIMBACH (*J. pr. Chem.*, 1902, [ii], 65, 20—41).—*Pyromucylhydrazide*,  $C_4OH_3 \cdot CO \cdot N_2H_3$ , prepared by boiling ethyl pyromucate with hydrazine hydrate, crystallises in prisms, melting and becoming brown at  $80^\circ$  and boiling and decomposing at  $279^\circ$ ; the *hydrochloride* crystallises in silky needles melting at  $178^\circ$ ; the *sodium* derivative forms a crystalline mass. *Pyromucylacetylhydrazide*,  $C_4OH_3 \cdot CO \cdot N_2H_2 \cdot COMe$ , prepared from the hydrazide and acetic anhydride, crystallises in leaflets with a silky lustre, melting at  $153.5^\circ$ ; *pyromucylbenzoylhydrazide*, prepared by boiling an alcoholic solution of the hydrazide, benzoyl chloride, and sodium hydroxide, crystallises in colourless leaflets melting at  $226^\circ$ . *Pyromucyl- $\beta$ -propylidenehydrazide*,  $C_4OH_3 \cdot CO \cdot N_2H \cdot CMe_2$ , crystallises in colourless plates melting at  $72^\circ$ ; *pyromucylbenzylidenehydrazide*,  
 $C_4OH_3 \cdot CO \cdot N_2H \cdot CHPh$ ,

in long needles, melting and decomposing at  $219^\circ$ . The *pyromucylhydrazide* of ethyl acetoacetate,  $C_4OH_3 \cdot CO \cdot N_2H \cdot CMe \cdot CH_2 \cdot CO_2Et$ , forms colourless needles melting at  $234^\circ$ .

*s-Dipyromucylhydrazide*,  $N_2H_2(CO \cdot C_4OH_3)_2$ , prepared by the action of iodine on an alcoholic solution of the hydrazide, crystallises in small, lustrous needles melting at  $232^\circ$ .

*Pyromucylazoimide*,  $C_4OH_3 \cdot CO \cdot N_3$ , prepared by adding sodium nitrite to a solution of the hydrazide in dilute acetic acid, crystallises in small, monoclinic plates melting at  $62.5^\circ$ . *Pyromucylanilide*,  
 $C_4OH_3 \cdot CO \cdot NHPh$ ,

prepared from the azoimide and aniline in alcoholic solution, crystallises in colourless needles melting at  $123.5^\circ$ .

*Ethyl furfurylcarbamate*,  $C_4OH_3 \cdot NH \cdot CO_2Et$ , prepared from the azoimide and boiling absolute alcohol, forms crystals, and boils at  $133^\circ$  under 24 mm. pressure and at  $215^\circ$  with decomposition under the ordinary pressure. *Methyl furfurylcarbamate*,  $C_4OH_3 \cdot NH \cdot CO_2Me$ , from the azoimide and methyl alcohol, is a yellow oil boiling at  $120^\circ$  under 20 mm. pressure. *Difurfurylcarbamide*,  $CO(NH \cdot C_4OH_3)_2$ , prepared with difficulty by warming pyromucylazoimide with moist benzene, forms a yellow, crystalline mass, melting and decomposing at about  $220^\circ$ .

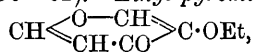
All attempts to prepare  $\alpha$ -furfurylamine from the urethane failed.

K. J. P. O.

**Hydrolysis of Pyromucylurethane.** By R. MARQUIS (*Compt. rend.*, 1902, 134, 288—289).—An account is given of preliminary and, at present, unsuccessful experiments on the formation of furfurylamine from pyromucylurethane by hydrolysis with alkalis (compare Leimbach, preceding abstract).

K. J. P. O.

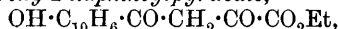
**Ethylpyromeconyl Ether.** By RICCARDO OLIVERI-TORTORICI (*Gazzetta*, 1902, 32, i, 56—62).—*Ethyl pyromeconyl ether*,





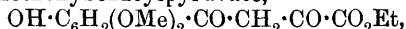
obtained by heating ethylcomenic acid, forms a colourless, unstable liquid boiling at  $220-221^{\circ}$ , and giving no coloration with ferric chloride. It has a faint phenolic odour and a neutral reaction, and is soluble in most organic solvents. It is not attacked either by cold nitric acid or by a chloroform solution of bromine, but alkalis readily dissolve it, assuming an intense yellow colour. When hydrolysed in presence of alkalis, it is resolved quantitatively into formic acid and acetolic ether,  $\text{CH}_2\text{Ac}\cdot\text{OEt}$ .  
T. H. P.

**$\alpha$ -Naphthachromone.** By STANISLAUS VON KOSTANECKI and G. FROEMSDORFF (*Ber.*, 1902, **35**, 859—861. Compare *Abstr.*, 1901, i, 735).—*Ethyl 1-hydroxy-2-naphthoylpyruvate*,



obtained by condensing 2-acetyl- $\alpha$ -naphthol with ethyl oxalate by means of sodium, crystallises from ethyl acetate in yellowish plates and melts at  $114^{\circ}$ ; when boiled with concentrated hydrochloric acid, it yields  *$\alpha$ -naphthachromonecarboxylic acid*,  $\text{C}_{10}\text{H}_6\left\langle\begin{array}{c} \text{O}-\text{C}\cdot\text{CO}_2\text{H} \\ \text{CO}\cdot\text{CH} \end{array}\right\rangle$ , which crystallises from glacial acetic acid in white needles, and melts at  $277-278^{\circ}$  forming  *$\alpha$ -naphthachromone*,  $\text{C}_{10}\text{H}_6\left\langle\begin{array}{c} \text{O}-\text{CH} \\ \text{CO}\cdot\text{CH} \end{array}\right\rangle$ . This separates from dilute alcohol in lustrous, efflorescent, white needles, and is hydrolysed by alcoholic sodium ethoxide to 2-acetyl- $\alpha$ -naphthol and formic acid.  
W. A. D.

**5:7-Dihydroxychromone.** By STANISLAUS VON KOSTANECKI and J. C. DE RUIJTER DE WILDT (*Ber.*, 1902, **35**, 861—865).—*Ethyl 2-hydroxy-4:6-dimethoxybenzoylpyruvate*,



obtained by condensing phloracetophenone dimethyl ether with ethyl oxalate by means of sodium, crystallises from alcohol in yellowish, rhombic plates, melts at  $149^{\circ}$ , and is converted by boiling hydrochloric acid of sp. gr. 1.19 into *5:7-dimethoxychromone-2-carboxylic acid*,  $\text{C}_6\text{H}_2(\text{OMe})_2\left\langle\begin{array}{c} \text{O}-\text{C}\cdot\text{CO}_2\text{H} \\ \text{CO}\cdot\text{CH} \end{array}\right\rangle$ , which separates from alcohol in colourless needles containing  $1\text{H}_2\text{O}$ ; the anhydrous substance melts at  $244.5^{\circ}$  and is transformed thereby with loss of carbon dioxide into *5:7-dimethoxychromone*,  $\text{C}_6\text{H}_2(\text{OMe})_2\left\langle\begin{array}{c} \text{O}-\text{CH} \\ \text{CO}\cdot\text{CH} \end{array}\right\rangle$ . This crystallises from water in white needles containing  $1\text{H}_2\text{O}$ , melts, when dry, at  $131-132^{\circ}$ , and, by boiling hydriodic acid, is converted into *5:7-dihydroxychromone*, which crystallises from alcohol in white plates and melts at  $273^{\circ}$ ; the latter, on being boiled with a methyl alcoholic solution of methyl iodide and potassium hydroxide, yields *5-hydroxy-7-methoxychromone*, which crystallises from alcohol in needles and melts at  $117-118^{\circ}$ ; the hydroxyl group in position 5 is protected by the adjacent carbonyl radicle, but on boiling the ether with acetic anhydride containing sodium acetate, it yields *5-acetoxy-7-methoxychromone*, which crystallises from dilute alcohol in long, lustrous needles and melts at  $141^{\circ}$ .

[With H. FEINSTEIN].—*Ethyl 2-hydroxy-4-methoxybenzoylpyruvate*,

$\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CO}_2\text{Et}$ , prepared from resacetophenone monomethyl ether and ethyl oxalate, crystallises from alcohol, melts at  $107-108^\circ$ , and with boiling hydrochloric acid yields 7-methoxychromone-2-carboxylic acid,  $\text{OMe} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{C} \cdot \text{CO}_2\text{H} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{CH} \end{smallmatrix}$ ; this crystallises from alcohol in needles and melts at  $261^\circ$ , being thereby converted into 7-methoxychromone, melting at  $110^\circ$ . W. A. D.

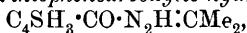
**Synthesis of 7-Hydroxy-2-benzylchromone.** By O. HANNACH and STANISLAUS VON KOSTANECKI (*Ber.*, 1902, 35, 866—868).—*ω*-Phenacetyl-2:4-diethoxyacetophenone,  $\text{C}_6\text{H}_3(\text{OEt})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2\text{Ph}$ , obtained by condensing resacetophenone diethyl ether with ethyl phenylacetate by means of sodium, crystallises from dilute alcohol in white leaflets, melts at  $75^\circ$ , and by boiling hydriodic acid of sp. gr. 1.96 is converted into 7-ethoxy-2-benzylchromone,  $\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{C} \cdot \text{CH}_2\text{Ph} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{CH} \end{smallmatrix}$ , which separates from alcohol in long, white needles, melts at  $154^\circ$ , and is hydrolysed by alcoholic sodium ethoxide into resacetophenone monoethyl ether and phenylacetic acid. 7-Hydroxy-2-benzylchromone, crystallises from alcohol in white prisms and melts at  $183^\circ$ ; 7-acetoxy-2-benzylchromone resembles it and melts at  $114^\circ$ . W. A. D.

**Dibromodinaphthaxanthonium Bromide and Di-iododinaphthaxanthonium Iodide and the Bromohydrin-dibromide and the Iodohydrin-di-iodide of the so-called Dinaphthylene Glycol.** By ROBERT FOSSE (*Compt. rend.*, 1902, 134, 177—179. Compare Abstr., 1901, i, 322, 384, 604, 643, and this vol., i, 51, 171).—Dibromodinaphthaxanthonium bromide,  $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{CHBr} \\ \diagup \quad \diagdown \\ \text{OBr}_2 \end{smallmatrix} \text{C}_{10}\text{H}_6$ , prepared by adding bromine to a glacial acetic acid solution of dinaphthaxanthonium bromide,  $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{OBr} \end{smallmatrix} \text{C}_{10}\text{H}_6$ , is also obtained by adding bromine to dinaphthaxanthen or to the bromohydrin of the so-called dinaphthylene glycol; it regenerates dinaphthaxanthen when boiled with alcohol, acetaldehyde and hydrogen bromide being simultaneously produced.

Di-iododinaphthaxanthonium iodide,  $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{CHI} \\ \diagup \quad \diagdown \\ \text{OI}_2 \end{smallmatrix} \text{C}_{10}\text{H}_6$ , obtained by adding iodine to a benzene solution of dinaphthaxanthen, crystallises in red needles; it may also be formed from the so-called naphthylene glycol. G. T. M.

**Hydrazides and Azoimides of Organic Acids. XXV. Hydrazide [and Azoimide] of *α*-Thiophencarboxylic Acid.** By THEODOR CURTIUS and HEINRICH THYSEN (*J. pr. Chem.*, 1902, [ii], 65, 1—19).—*α*-Thiophencarboxylic hydrazide,  $\text{C}_4\text{SH}_3 \cdot \text{CO} \cdot \text{N}_2\text{H}_3$ , prepared by long boiling of ethyl *α*-thiophencarboxylate with hydrazine hydrate, crystallises in long needles, melts at  $136^\circ$  and exhibits the usual properties of the hydrazides; the hydrochloride forms small, white needles melting and decomposing at  $247^\circ$ . The sodium derivative of the hydrazide is a yellow precipitate.

*Benzylidene- $\alpha$ -thiophencarboxylic hydrazide*,  $C_4SH_3 \cdot CO \cdot N_2H \cdot CHPh$ , prepared from the hydrazide and benzaldehyde, crystallises in lustrous needles melting at  $177^\circ$ . *o-Hydroxybenzylidene- $\alpha$ -thiophencarboxylic hydrazide*,  $C_4SH_3 \cdot CO \cdot N_2H \cdot CH \cdot C_6H_4(OH)$ , crystallises in yellow needles melting at  $176^\circ$ ; the compound obtained from ethyl acetoacetate and the hydrazide,  $C_4SH_3 \cdot CO \cdot N_2H \cdot CMe \cdot CH_2 \cdot CO_2Et$ , forms crystals melting at  $112^\circ$ ;  *$\beta$ -propylidene- $\alpha$ -thiophencarboxylic hydrazide*,



prepared from acetone and the hydrazide, forms crystals melting at  $108^\circ$ ;  *$\alpha$ -thiophencarboxylic acetylhydrazide*,  $C_4SH_3 \cdot CO \cdot N_2H_2 \cdot COMe$ , forms crystals melting at  $172^\circ$ ;  *$\alpha$ -thiophencarboxylic benzoylhydrazide*,  $C_4SH_3 \cdot CO \cdot N_2H_2 \cdot COPh$ , is prepared by the Schotten-Baumann method. *s-Dithiophencarboxylic hydrazide*,  $N_2H_2(CO \cdot C_4SH_3)_2$ , prepared by the action of iodine on an alcoholic solution of the hydrazide, forms crystals melting at  $262^\circ$ .

*$\alpha$ -Thiophencarboxylic azoimide*,  $C_4SH_3 \cdot CO \cdot N_3$ , prepared by careful addition of sulphuric acid to a solution containing the hydrazide and sodium nitrite, forms a yellow, crystalline mass melting at  $37^\circ$ .

*$\alpha$ -Thiophencarboxylic anilide*,  $C_4SH_3 \cdot CO \cdot NHPh$ , prepared from the azoimide and aniline, crystallises in leaflets melting at  $140^\circ$  and is identical with the substance prepared from phenylcarbimide, thiophen and aluminium chloride (Leuckart and Schmidt, Abstr., 1885, 1224).

*s-Phenyl- $\alpha$ -thiophencarbamide*,  $NHPh \cdot CO \cdot NH \cdot C_4SH_3$ , prepared by heating the azoimide with aniline, crystallises in needles melting and decomposing at  $215^\circ$ .  *$\alpha$ -Thiophenurethane*,  $C_4SH_3 \cdot NH \cdot CO_2Et$ , prepared by boiling the azoimide with absolute alcohol, crystallises in lustrous, colourless needles melting at  $48^\circ$ . *s-Di- $\alpha$ -thiophencarbamide*,  $CO(NH \cdot C_4SH_3)_2$ , prepared by warming the azoimide with water, crystallises in brownish or greyish-violet needles melting at  $224^\circ$ . All attempts to prepare  $\alpha$ -thiophenamine from the urethane failed.

K. J. P. O.

**Oxidation of  $\alpha$ -isoCinchonine.** By ZDENKO H. SKRAUP and R. ZWGER (Monatsh., 1901, 22, 1083—1096. Compare Abstr., 1900, i, 605).— $\alpha$ -isoCinchonine, when treated with methyl iodide, yields a stable *methiodide* melting at  $252$ — $253^\circ$ . By treatment of  $\alpha$ -isocinchonine hydriodide with methyl iodide, the hydriodide of an isomeric methiodide, melting at  $247$ — $248^\circ$ , is obtained. This methiodide decomposes, however, when attempts are made to liberate it from its salt.

When oxidised with chromic acid,  $\alpha$ -isocinchonine yields carbon dioxide and formic, acetic, and cinchonic acids. No substance analogous to meroquinine could be isolated. Small quantities of two products,  $C_{10}H_{15}O_5N$ , perhaps a hydroxypiperidinebutyric acid, and  $C_6H_{16}O_5NCl$ , which might be a chloropiperidinecarboxylic acid containing  $3H_2O$ , were isolated in the form of the platinichlorides. The formation of cinchonic acid shows that the quinoline nucleus of cinchonine is present in the same form in  $\alpha$ -isocinchonine. G. Y.

**Physical Properties of  $\alpha$ - and  $\beta$ -isoCinchonine.** By ZDENKO H. SKRAUP (Monatsh., 1901, 22, 1097—1102. See Abstr., 1900, i, 606).— $\alpha$ - and  $\beta$ -isoCinchonine are best purified by crystallisation from petroleum

of low boiling point and have then practically identical melting points;  $\alpha$ -isocinchonine melted at  $126-126.5^\circ$ ,  $\beta$ -isocinchonine at  $126-127^\circ$ . The bases are heteromorphous and pseudorhombic.  $\alpha$ -isocinchonine was found to have  $[\alpha]_D + 49.54^\circ$ ;  $+ 49.74^\circ$ ;  $+ 51.77^\circ$ ;  $+ 51.85^\circ$ .  $\beta$ -isocinchonine at similar concentrations had  $[\alpha]_D - 62.14^\circ$ ;  $- 57.85^\circ$ ;  $- 58.26^\circ$ ;  $- 59.81^\circ$ . The bases are therefore not enantiomorphous forms. G. Y.

**Cinchonifine, Cinchotine, and Cinchonine.** By ZDENKO H. SKRAUP (*Monatsh.*, 1901, 22, 1103—1104).—The facts contained in Jungfleisch and Léger's papers (Abstr., 1901, i, 287, 338) have previously been published by other authors. G. Y.

**Decomposition of Cocaine Hydrochloride in Alcoholic Solution by Hydrogen Chloride.** By PAUL HORST (*Chem. Zeit.*, 1902, 26, 27—28).—As the result of several experiments, the author concludes that the formation of methyl benzoate in the decomposition of cocaine by mineral acids or alcoholic potash is due to secondary reactions, methyl alcohol being split off from the cocaine and combining with the benzoic acid which also results from the hydrolysis. A. F.

**Ecgonine.** By OSWALD HESSE (*J. pr. Chem.*, 1902, [ii], 65, 91—95).—It has been stated by Gintl and Storch (*Monatsh.*, 1887, 8, 79) that when ecgonine is heated with methyl iodide and methyl alcohol at  $100^\circ$ , an additive compound,  $C_9H_{15}O_3N, MeI$ , is formed. The author is, however, of opinion that the platinichloride, which they described, resembled rather that of ecgonine itself than that of the additive compound.

If ecgonine is heated with methyl iodide and methyl alcohol under a reflux condenser, ecgonine methiodide,  $C_9H_{15}O_3N, MeI, H_2O$ , is obtained, which crystallises in colourless prisms, melts at  $218^\circ$ , and is easily soluble in water and fairly so in alcohol; when it is heated with hydriodic acid according to Zeisel's method, methyl iodide is not produced. The *methochloride* crystallises in large, colourless tablets containing  $1H_2O$ ; the *aurichloride* crystallises with  $1H_2O$ , which it loses at  $90^\circ$ , and melts at  $130^\circ$ ; the *platinichloride* also crystallises with  $1H_2O$  and melts at  $194^\circ$ . The *hydroxide* crystallises in colourless prisms with  $1H_2O$ , dissolves readily in water, and has  $[\alpha]_D - 42.4^\circ$ ; by the action of benzoyl chloride on it, benzoyl ecgonine *methochloride* is obtained, which crystallises in colourless plates.

*Ecgonine ethiodide* crystallises in colourless prisms containing  $2H_2O$ ; when slowly heated, it loses its water of crystallisation at  $160^\circ$  and melts at  $192^\circ$ , but if heated rapidly it melts at about  $185^\circ$ . The *hydroxide* forms long, colourless prisms containing  $1H_2O$ , which is eliminated at  $120^\circ$ ; it melts and decomposes at  $202^\circ$ ; its aqueous solution is of neutral reaction. E. G.

**Corydalis Alkaloids.** By JOHANNES GADAMER, with H. ZIEGENBEIN and H. WAGNER (*Arch. Pharm.*, 1902, 240, 19—52. Compare Abstr., 1901, i, 288; Trans., 1894, 65, 25; 1901, 79, 87).—By an improved method of extraction, more than 400 grams of alkaloids,

including some new ones, have been obtained from 10 kilos. of the tubers of *Corydalis cava*. There were obtained: (i) in ethereal solution; A, crystalline bases which were separated by fractional extraction with alcohol, whereby corydaline, bulbocapnine, corycavine and corybulbine were obtained in this order; B, an amorphous mixture of bases, which were converted into hydrobromides and precipitated fractionally with ammonia, when there were obtained in the following order, beginning with the weakest base, *a* (crystalline), corydaline, corybulbine, *isocorybulbine*, *corycavamine*, corycavine, *corydine*, bulbocapnine, and a base melting at  $135^{\circ}$  of unknown strength; *b* (amorphous), 1, a base of medium strength, forming a crystalline hydrochloride; 2, a mixture of amorphous bases forming amorphous salts. (ii) Insoluble in ether, precipitated by chloroform from the strong ammoniacal aqueous solution, corytuberine. Protopine was not detected.

The crystalline bases fall into three groups. 1, Corydaline, corybulbine and *isocorybulbine*; weak bases, oxidised by alcoholic iodine solution to compounds resembling berberine. 2, Corycavine and corycavamine; bases of medium strength, attacked by iodine solutions. 3. Bulbocapnine, corydine, and corytuberine; strong bases, oxidised by iodine solution but yielding no well characterised products (probably owing to the presence of the free hydroxyl group).

The action of these alkaloids on an alcoholic iodine solution (the digestion was continued for 3 hours at  $100^{\circ}$ ) cannot be used for purposes of quantitative estimation. Under these circumstances, the iodine attacks the alcohol to some extent; and, although the addition of hydriodic acid retards this action, it also retards the action on the alkaloid.

When corydaline is dissolved in strong sulphuric acid and the solution allowed to remain for a day at the ordinary temperature, *corydalinesulphonic acid*,  $C_{22}H_{26}O_4N \cdot SO_3H$ , is formed. This melts above  $260^{\circ}$ , is insoluble in water, and forms an amorphous *potassium* salt.

When corydaline is oxidised with alcoholic iodine and the product reduced with zinc and dilute sulphuric acid, optically inactive corydaline is obtained; most of it melts at  $134$ – $135^{\circ}$ , but occasionally some melted at  $156$ – $157^{\circ}$ . The first variety could not be separated into active components, and therefore is probably *i*-corydaline, inactive by internal compensation. By crystallising the bromo-camphorsulphonate of the second variety from water, a partial separation was effected, the alkaloid regenerated from the crystals being dextrorotatory in chloroform solution; this variety may, therefore, be regarded as the racemic form, *r*-corydaline.

*isocorybulbine*,  $C_{21}H_{25}O_4N$  or  $C_{18}H_{16}ON(OMe)_3$ , melts at  $179$ – $180^{\circ}$  and is very sensitive to light. C. F. B.

**Laudanine.** By OSWALD HESSE (*J. pr. Chem.*, 1902, [ii], 65, 42–45. Compare Abstr., 1895, i, 110).—The author has previously suggested (*loc. cit.*) that laudanoline is the methyl ether of laudanine; the latter contains three methoxy-groups and one hydroxyl, and forms a *sodium* salt,  $C_{20}H_{24}O_4NNa \cdot 4H_2O$ , which crystallises in small, white

prisms. On treating the alkaloid or the sodium salt with methyl iodide in cold methyl alcohol, a small amount of *r*-laudanone is obtained, which forms white crystals insoluble in alkalis. With ethyl iodide, 80 per cent. of an *ethyl* ether of laudanone,  $C_{20}H_{24}O_4 \cdot \text{Net}$ , is obtained as an amorphous mass, which melts at  $40-50^\circ$ , is alkaline in reaction, and gives no colour reaction with ferric chloride. The *hydrochloride* crystallises, with  $5H_2O$ , in colourless prisms; the *platinichloride*, with  $2H_2O$ , is a yellow, crystalline precipitate. K. J. P. O.

**New Derivatives of Bismuth Chloride and Iodide.** By LUDWIG VANINO and OTTO HAUSER (*Ber.*, 1902, 35, 663—666. Compare Abstr., 1901, i, 289).—*Bismuth iodide pyridine hydrochloride*,  $\text{BiI}_3 \cdot \text{C}_5\text{NH}_5 \cdot \text{HCl}$ , obtained by dissolving bismuth pyridine iodide in dilute hydrochloric acid, crystallises in ruby-red prisms. The *salt*,  $2\text{BiI}_3 \cdot 3\text{C}_5\text{NH}_5 \cdot \text{HI}$ , obtained by dissolving the compound  $2\text{BiI}_3 \cdot 3\text{C}_5\text{NH}_5$  in an excess of hydriodic acid of sp. gr. 1.7, forms red crystals and is not affected by hydrogen chloride; the *quinoline salt*,  $\text{BiI}_3 \cdot \text{C}_9\text{NH}_7 \cdot \text{HI}$ , obtained similarly from bismuth quinoline chloride, closely resembles the pyridine compound, but is decomposed by hydrogen chloride and dissolves in hydrobromic acid, giving the compound  $\text{BiI}_3 \cdot \text{C}_9\text{NH}_7 \cdot \text{HBr}$ ; this forms bright orange, silky crystals.

*Bismuth diethylaniline chloride*,  $\text{BiCl}_3 \cdot 2\text{Net}_2\text{Ph} \cdot \text{HCl}$ , forms large, white crystals, and *bismuth dimethylaniline chloride*,



small prisms; the *salt*,  $\text{BiCl}_3 \cdot 3\text{Net}_2\text{Ph} \cdot \text{HCl}$ , also crystallises well. These compounds are not hygroscopic and are only slowly decomposed by water. W. A. D.

**Some Compounds of Pyridine with Cupric and Cuprous Thiocyanates.** By FRANZ M. LITTERSCHEID (*Arch. Pharm.*, 1902, 240, 74—77. Compare Abstr., 1901, i, 635).—When freshly precipitated cupric thiocyanate is dissolved in boiling pyridine and the solution allowed to cool, lustrous, green crystals of a compound,  $\text{Cu}(\text{C}_5\text{NH}_5 \cdot \text{CNS})_2 \cdot 2\text{C}_5\text{NH}_5$ , separate. These lose pyridine when warmed with water or kept in the air, forming the compound  $\text{Cu}(\text{C}_5\text{NH}_5 \cdot \text{CNS})_2$ , which is coloured a brighter green.

When cupric thiocyanate is dissolved in excess of pyridine and sulphur dioxide is passed into the hot solution, a colourless compound,  $\text{Cu}_2(\text{C}_5\text{NH}_5 \cdot \text{CNS})_2 \cdot \text{C}_5\text{NH}_5$ , separates; this readily loses pyridine, forming a compound,  $\text{Cu}_2(\text{C}_5\text{NH}_5 \cdot \text{CNS})_2$ , which can also be obtained by treating freshly precipitated cuprous thiocyanate with pyridine; this compound is decomposed when boiled with pyridine, the cupric compound being formed.

Cuprosocupric thiocyanate does not form a compound with pyridine; a mixture of cupric and cuprous compounds is obtained instead.

C. F. B.

**Action of Acetyl Chloride, Benzoyl Chloride, and Ethylidenelactic Acid on Pyridinecholine.** By [ERNST SCHMIDT and] FRANZ M. LITTERSCHEID (*Arch. Pharm.*, 1902, 240, 77—80. Compare Nothnagel, Abstr., 1894, i, 437).—When pyridinecholine chloride

(Roithner, Abstr., 1895, i, 319) is heated with acetyl chloride for 3 hours, it is partly converted into *acetylpyridinecholine chloride*,  $C_5NH_5Cl \cdot CH_2 \cdot CH_2 \cdot OAc$ , of which the *platinichloride* and *aureichloride* melt at  $193-194^\circ$  and  $143-144^\circ$  respectively. When boiled for 2 hours with benzoyl chloride, it is converted entirely into *benzoylpyridinecholine chloride*,  $C_5NH_5Cl \cdot CH_2 \cdot CH_2 \cdot OBz$ , the *platinichloride* and *aureichloride* of which melt at  $201^\circ$  and  $128-129^\circ$  respectively. With lactic acid, it will not combine.

C. F. B.

**The Carbon Double Linking and the Carbonyl Radicle.** By DANIEL VORLÄNDER (*Annalen*, 1902, 320, 66-98).—Radicles, when attached to carbonyl, acquire properties differing considerably from those which they possess in other states of combination. The hydroxyl and chlorine radicles of the organic acids and their chlorides have properties which are not manifested by these radicles when combined with alkyl groups. If this alteration in the properties of a group attached to carbonyl is general, then the carbon residue of the double linking in an  $\alpha$ -unsaturated compound should vary in its reactivity according as to whether it is attached to carbonyl or not. The hydroxyl radicle when united with carbonyl, is distinguished from the group in other combinations by a marked increase in the electrochemical difference between its oxygen and hydrogen atoms; a similar, but less appreciable, difference is noticed between the electrical condition of the two carbon atoms of the double linking contiguous to carbonyl, the state of the two configurations being typified by the formulæ  $HO \cdot C^+ \cdot O^-$  and  $C^+ \cdot C^- \cdot C^+ \cdot O^-$  respectively. Accordingly, the addition of the compound  $HR$  leads to the formation of the additive product  $CR \cdot CH \cdot C^+ \cdot O^-$ , and not to that of the isomeride  $CH \cdot CR \cdot C^+ \cdot O^-$ .

The interpolation of a methylene residue between the carbonyl group and the substituent radicle or double linking completely annuls this variation in electrical condition, and a substance containing the residue  $HO \cdot CH_2 \cdot CO$  behaves like an ordinary alcohol, whilst the double linking in the configuration  $C^+ \cdot C^- \cdot CH_2 \cdot CO$  is destitute of the reactivity which it possesses in the  $\alpha$ -ketones.

The reactivity of the  $\alpha\beta$ -double linking in ethyl cinnamylidenemalonate,  $CHPh \cdot CH \cdot CH \cdot CH(CO_2Et)_2$ , towards hydrogen cyanide follows from the preceding generalisations, but there is also some evidence indicating that the  $\gamma\delta$ -double linking also reacts with this reagent, for a fully saturated tricarboxylic acid was obtained as the ultimate product of hydrolysis (Thiele and Meisenheimer, Abstr., 1899, i, 603).

These considerations justify the belief that the reactivity of the double linking of  $\alpha$ -unsaturated ketones and esters is due to that property of carbonyl which brings about the increased mobility of the hydroxyl and chlorine radicles of the organic acids and their chlorides. This view is opposed to Thiele's theory of partial valency as applied to the explanation of these changes; for, according to this hypothesis, it is the ends of the system  $C^+ \cdot C^- \cdot C^+ \cdot O^-$  which are reactive, so that with the reagent  $HR$ , the primary additive product is  $CR \cdot C^+ \cdot C^- \cdot OH$ , this enolic substance subsequently changing into its ketonic form. The results

set forth in the experimental portion of the communication indicate that the increased activity of the double linking is not due to the negative character of the carbonyl group, for the reactivity of the amides  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NHR}$  and  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NR}_2$  towards ethyl sodiomalonate is even greater than that of the esters

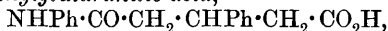


and moreover there is no apparent connection between the reactivity of the amide and the strength of the corresponding amine, the amount of interaction occurring with the piperidide being scarcely greater than that noticed in the case of the diphenylamide, in spite of the enormous difference between the strengths of piperidine and diphenylamine.

[With P. HERRMANN.]—A solution of ethyl sodiomalonate in ethyl alcohol is employed as the reagent for testing the reactivity of the double linking. Additive products were not obtained with the following unsaturated compounds: styrene, stilbene, nitrophenylethylene, diphenylbutadiene, pyrrole, N-phenylpyrrole, benzylidenequinoline, cinnamylidenephénylhydrazine, and benzylideneacetone phenylhydrazine; these substances are alike in not containing a carbonyl group. Cinnamide readily reacts with ethyl sodiomalonate, yielding the compound  $\text{CO}\langle\begin{smallmatrix} \text{NH} & \text{CO} \\ \text{CH}_2 & \text{CHPh} \end{smallmatrix}\rangle\text{CH}\cdot\text{CO}_2\text{Et}$ , which crystallises from water in needles and melts at  $119^\circ$ ; this product, when hydrolysed with hydrochloric acid, yields  $\beta$ -phenylglutaric acid.

Ethyl cinnamate reacts in a similar manner, but the additive compound is unstable, and is readily hydrolysed to  $\beta$ -phenylglutaric acid; this product being characterised by means of its *methyl* ester, which crystallises in white needles melting at  $86$ – $87^\circ$ , and its anhydride, which boils at  $217$ – $219^\circ$  under 15 mm. pressure and melts at  $105^\circ$ ; the mean electrical conductivity of the acid is  $0.00772$ .

$\beta$ -Phenylglutarimide,  $\text{CHPh}\langle\begin{smallmatrix} \text{CH}_2 & \text{CO} \\ \text{CH}_2 & \text{CO} \end{smallmatrix}\rangle\text{NH}$ , formed by heating the acid in a stream of ammonia gas, crystallises in leaflets and melts at  $173$ – $174^\circ$ ;  $\beta$ -phenylglutaranilic acid,



produced by mixing the anhydride with aniline, crystallises from alcohol in white needles and melts at  $171^\circ$ . The methylamide, dimethylamide, ethylamide, and diethylamide of cinnamic acid all react with ethyl sodiomalonate, the additive products were not isolated, however, but hydrolysed to  $\beta$ -phenylglutaric acid; the reactions were never complete, and the weight of unaltered amide was estimated in each experiment.

The diethylamide and piperidide of  $\alpha\beta$ -dibromo- $\beta$ -phenylpropionic acid, prepared by adding bromine to the corresponding amide and piperidide, crystallise respectively in prisms melting at  $127^\circ$  and in needles decomposing at  $189^\circ$ .

The acid,  $\text{C}_5\text{NH}_{10}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}(\text{CO}_2\text{H})_2$ , results from the interaction of the piperidide of cinnamic acid and ethyl sodiomalonate after treating the mixture with mineral acid; it crystallises from ethyl acetate or water in white prisms melting at  $146^\circ$  with evolution of carbon dioxide; the fused product then consists of the *semipiperidide*,  $\text{C}_5\text{NH}_{10}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , of  $\beta$ -phenylglutaric acid, and a

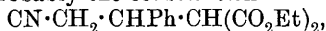


substance which yields this acid on hydrolysis with hot hydrochloric acid.

The diphenylamide of cinnamic acid reacts with ethyl sodiomalonate, and the additive compound on hydrolysis ultimately yields  $\beta$ -phenylglutaric acid.

Cinnamanilide, when treated with ethyl sodiomalonate, gives rise to the ester  $\text{CO} \begin{smallmatrix} \text{NPh} \text{---} \text{CO} \\ \text{CH}_2 \cdot \text{CHPh} \end{smallmatrix} \text{CH} \cdot \text{CO}_2\text{Et}$ , which crystallises from alcohol in white needles and melts at  $166^\circ$ , and also to the sodium salt of the acid  $\text{NHPh} \cdot \text{CO} \cdot \text{CH} \cdot \text{CHPh} \cdot \text{CH}(\text{CO}_2\text{Et}) \cdot \text{CO}_2\text{H}$ ; both these substances, when hydrolysed with cold alcoholic potassium hydroxide solution, yield the dicarboxylic acid,  $\text{NHPh} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{CH}(\text{CO}_2\text{H})_2$ , this substance, when heated, furnishing phenylglutaranilic acid. Both the products of the preceding reaction, when hydrolysed with boiling hydrochloric acid, yield  $\beta$ -phenylglutaric acid.

Cinnamitrile and ethyl sodiomalonate interact, the product being a viscid oil having probably the constitution



which, on hydrolysis with hydrochloric acid, ultimately gives rise to  $\beta$ -phenylglutaric acid.

G. T. M.

**5-Chloro- and 5-Bromo-acridine.** KALLE & Co. (D.R.-P. 122607).—5 Chloroacridine, already obtained by Graebe and Lagodzinski from acridone and phosphorus pentachloride (Abstr., 1893, i, 649), is prepared by heating thioacridone with phosphorus pentachloride and phosphorus oxychloride at  $120\text{--}125^\circ$ .

**5-Bromoacridine**,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CBr} \\ | \\ \text{N} \text{---} \end{smallmatrix} \text{C}_6\text{H}_4$ , produced by treating thioacridone with red phosphorus and bromine, and extracting the product with 30—40 per cent. sulphuric acid, melts at  $116\text{--}117^\circ$ ; it is accompanied by another basic substance melting at  $255^\circ$ , which is insoluble in ether.

G. T. M.

**$\psi$ -Ammonium Bases and their Derivatives.** By ARTHUR HANTZSCH and ARTHUR HORN (*Ber.*, 1902, 35, 877—883).—The reversion of ammonium hydroxide bases to alcoholic  $\psi$ -bases and of their salt-like cyanides to the organic cyanides of the  $\psi$ -bases in the acridinium series (Hantzsch and Kalb, Abstr., 1899, i, 400; 1900, i, 113) is paralleled by the behaviour of the thiols  $\text{:NMe} \cdot \text{SH}$  and their ethers  $\text{:NMe} \cdot \text{SPh}$ , which immediately revert to derivatives of the  $\psi$ -base.

**5-Phenyl-10-methylthioacridol**,  $\text{NMe} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CPh} \cdot \text{SH}$ , prepared from phenylmethylacridinium chloride and sodium hydrogen sulphide, is a yellowish-white substance which melts at  $105\text{--}109^\circ$ , is insoluble in water, slightly soluble in alcohol, and readily so in benzene and carbon disulphide, thus resembling the mercaptans rather than the metallic sulphides; it is readily decomposed into hydrogen sulphide and phenylmethylacridol. The *phenyl ether*,  $\text{NMe} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CPh} \cdot \text{SPh}$ , from the acridinium chloride and sodium thiophenol, is a greyish-

yellow substance, soluble in alcohol, benzene, or chloroform, and is readily hydrolysed to thiophenol and phenylmethylacridol.

On the other hand, phenylmethylacridinium chloride and acridol both give, with sodium toluenesulphinate, a true *sulphinate*,  $\text{CPh} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} \text{NMe} \cdot \text{SO}_2 \cdot \text{C}_7\text{H}_7$ , which forms golden-yellow spangles, melts at  $208^\circ$ , and dissolves readily in water and alcohol, but not in benzene, ether, or chloroform; the isomeric sulphone of the  $\psi$ -base could not be prepared.

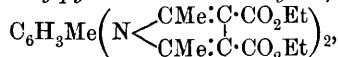
T. M. L.

#### Action of Aluminium Chloride on Phenylenediamine Nitrate.

By EMILIO GABUTTI (*L'Orosi*, 1901, **24**, 366—368).—*m*-Phenylenediamine nitrate,  $\text{C}_6\text{H}_4(\text{NH}_2)_2 \cdot 2\text{HNO}_3$ , forms large, shining crystals, readily soluble in water or alcohol. When heated with aluminium chloride, it yields a *m*-phenylenenitrodiamine,  $\text{C}_6\text{H}_4(\text{NH} \cdot \text{NO}_2)_2$ , which is obtained as a pale yellow oil with a characteristic odour and a strong acid reaction; it boils and violently explodes at  $90^\circ$ , and is soluble in ether.

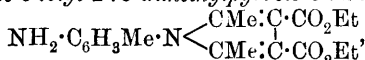
T. H. P.

Relative Basicity of the two Amino-groups in Substituted Diamines. III. *p*-Tolylenediamine [ $\text{CH}_3 : \text{NH}_2 : \text{NH}_2 = 1 : 2 : 5$ ]. By CARL BÜLOW and GEORG LIST (*Ber.*, 1902, **35**, 681—688).—*Ethyl p*-tolylene-bis-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate,



prepared by the interaction of *p*-tolylenediamine hydrochloride and ethyl diacetylsuccinate, crystallises from dilute alcohol in minute scales, melts at  $134^\circ$ , and gives the pyrrole reaction with a pine-splinter. The acid,  $\text{C}_{23}\text{H}_{22}\text{O}_8\text{N}_2$ , crystallises from dilute alcohol and melts at  $275^\circ$  with liberation of carbon dioxide. The acid silver salt,  $\text{C}_{23}\text{H}_{20}\text{O}_8\text{N}_2\text{Ag}_2$ , is a reddish-white powder.

*Ethyl 1-m-amino-o-tolyl-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate*,



crystallises from alcohol in long, slender, grey needles, melts at  $105$ — $106^\circ$ , and shows the pine-splinter reaction; the free amino-group can be diazotised and the product condensed to an azo-dye with  $\beta$ -naphthol-3 : 6-disulphonic acid. In order to determine with which amino-group condensation had taken place, the compound was diazotised and the product identified with that from *o*-toluidine and ethyl diacetylsuccinate; 1-*o*-tolyl-2 : 5-dimethylpyrrole-3 : 4-dicarboxylic acid,  $\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}$ , crystallises from alcohol in reddish, prismatic forms, melts at  $203$ — $204^\circ$  with liberation of carbon dioxide, and shows the pine-splinter reaction; the acid silver salt was prepared and analysed.

1-*m*-Tolyl-2 : 5-dimethylpyrrole-3 : 4-dicarboxylic acid, from *m*-toluidine and ethyl diacetylsuccinate, melts and decomposes at  $222$ — $223^\circ$ ; the acid silver salt was analysed.

1-*m*-Tolyl-2 : 5-dimethylpyrrole, prepared by distilling the preceding acid under slightly reduced pressure, crystallises from ether, melts at  $53^\circ$ , and is volatile in a current of steam.

T. M. L.

**Nitro- and Amino-derivatives of the Xylenes.** By EMILIO NOELTING and G. THESMAR (*Ber.*, 1902, **35**, 628—650. Compare Abstr., 1901, i, 588).—4 : 6-*Dinitro-2-acetylamino-m-xylene*, obtained by nitrating at 0° acetyl-2-*m*-xylidide dissolved in concentrated sulphuric acid, crystallises in white needles, melts and decomposes at 226—228°, and on hydrolysis with concentrated hydrochloric acid yields 4 : 6-*dinitro-2-amino-m-xylene*; this crystallises from alcohol in small, yellow leaflets, melts at 174—175°, and is reduced by ammonium sulphide to 6-*nitro-2 : 4-diamino-m-xylene*, which separates from boiling water in long, slender, orange-coloured needles and melts at 151—152°.

The nitration of 4-*nitro-o-xylene* dissolved in concentrated sulphuric acid with a mixture of sulphuric and nitric acids takes place at the ordinary temperature, and is completed by warming for 10 minutes on the water-bath; the product is a mixture of 4 : 5-*dinitro-* and 4 : 6-*dinitro-o-xylenes*, which can be separated by fractional crystallisation from alcohol. 4 : 5-*Dinitro-o-xylene* is the more sparingly soluble and crystallises in slender, white needles melting at 115—116°; it differs from its congener in being easily converted by alcoholic ammonia at 150° into 5-*nitro-4-amino-o-xylene*. This fact can be utilised in isolating 4 : 6-*dinitro-o-xylene*, which crystallises in white needles, melts at 75—76°, is reduced by ammonium sulphide to 6-*nitro-4-amino-o-xylene* (m. p. 74—75°) and by tin and hydrochloric acid to *o*-xylylene-*m*-diamine.

The nitration of 3-*nitro-o-xylene* yields a complex mixture, and an attempt to obtain a trinitro-*o-xylene* by energetically nitrating *o-xylene* gave only a mixture of dinitro-derivatives; Drossbach's trinitro-compound melting at 178° is really trinitro-*m-xylene*, derived from *m-xylene* present as an impurity.

A table is given differentiating the eleven xylylenediamines by their behaviour with ferric chloride, potassium dichromate, sodium nitrite, and bleaching powder; the diamines are best obtained by the reduction of the corresponding nitroxylidines with zinc dust in neutral solution according to Bamberger's method, and when pure do not become coloured on keeping. 3 : 4-*Diacetylamino-o-xylene* crystallises from benzene in small, white needles, and melts at 196—197°; 4 : 5-, 3 : 5-, and 3 : 6-*diacetylamino-o-xylenes* are similar, and melt respectively at 227—228°, 240—241°, and 275—276°. 2 : 5-*Diamino-m-xylene*, obtained by reducing the azo-compound from 2-*m*-xylidine and diazobenzene-*m*-sulphonic acid, crystallises from a mixture of benzene and light petroleum in nacreous leaflets and melts at 103—104°.

The following azines were prepared from the *o*-diamines by means of phenanthraquinone. 1 : 2-*Xylophenanthrazine* forms small, yellow needles melting at 223—224°; 2 : 3-*xylophenanthrazine*, brownish-yellow leaflets melting at 291—292°; 1 : 3- and 1 : 4-*xylophenanthrazine*, flat, yellowish needles melting at 206—207° and 285—286° respectively.

*s*-Xylylene-*o*-diamine interacts in dilute aqueous acetic acid solution with bleaching powder at 0°, giving 1 : 2-*xylo-4 : 5-quinonedichlorodimide*,  $C_6H_2Me_2(NCl)_2$ , which crystallises from ether in long, bright yellow needles, darkens at 70°, and explodes at 87°; it decomposes

rapidly at the ordinary temperature, becoming black in 24 hours. Attempts to obtain similar quinoneimides from other xylylene-*o*-diamines gave yellow powders which, although more stable, could not be crystallised and had no definite composition.

The following chrysoidines were prepared from the corresponding *m*-diamines. 3:5-Diamino-*o*-xylene-6-azobenzene, obtained from *o*-xylene-*m*-diamine, crystallises from dilute alcohol in long, scarlet-red needles and melts at 127°; 3:5-diamino-*o*-xylene-4-azobenzene, which is produced simultaneously, forms bright red leaflets, melts at 171—172°, and has little tinctorial power. 4:6-Diamino-*m*-xylene-5-azobenzene crystallises in red leaflets, 2:4-diamino-*m*-xylene-5-azobenzene in scarlet needles melting at 97.5—98°, and 3:5-diamino-*p*-xylene-2-azobenzene in orange needles melting at 90—91°.

The following eurhodines were prepared by the aid of *p*-nitroso-dimethylaniline hydrochloride. 3'-Dimethylaminopheno-3-amino-1:2-xylazine,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_3 \llbracket \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \rrbracket \text{C}_6\text{HMe}_2 \cdot \text{NH}_2$ , forms yellow needles and melts and decomposes at 265°; 3'-dimethylaminopheno-3-amino-2:4-xylazine crystallises in brownish-red needles melting at 241—242°, and 3'-dimethylaminopheno-3-amino-1:4-xylazine in small, yellow needles melting at 215—216°.

1:2-Xylo-3:6-quinonedichlorodiimide crystallises from dilute alcohol in slender, yellow needles and melts at 105.5°; 1:3-xylo-2:5-quinone-dichlorodiimide is similar, melts at 112°, and decomposes at 175°; 1:4-xylo-2:5-quinonedichlorodiimide forms slender, slightly brown needles melting at 124° and decomposing at 137°.

*o*-, *m*-, and *p*-Xylosafranines were prepared from the corresponding *p*-diamines. W. A. D.

5:4'-Dichloro-2-aminodiphenylamine. By E. WILBERG (*Ber.*, 1902, 35, 954—959).—5:4'-Dichloro-2-aminodiphenylamine, obtained when di-*p*-dichlorohydrazobenzene is treated with stannous chloride and hydrochloric acid, crystallises from benzene and light petroleum in small, white needles, and melts at 91°. It forms with carbon disulphide a thiocarbamide melting at 273°, with benzil, a stilbazonium compound melting at 213°, and with nitrous acid, an azoimide melting at 204°. The hydrochloride crystallises in slender, white needles and, when heated with water in a sealed tube at 200°, yields *p*-chloroaniline and 4'-chloro-2-aminodiphenylamine, which crystallises in long, white needles, melts at 119°, and forms an azoimide melting at 154°. 4'-Chloro-2-aminodiphenylamine can also be obtained by the reduction of 4'-chloro-2-nitrodiphenylamine, which is obtained by heating a mixture of *o*-chloronitrobenzene, *p*-chloroaniline, and sodium acetate at 170—190° for 10 hours and crystallises in long, orange-red needles melting at 145.5°. 5:4-Dichloro-2-aminodiphenylamine hydrochloride, when heated at 230—235° for 10 minutes, yields a fluorindine,  $\text{C}_{36}\text{H}_{21}\text{N}_5\text{Cl}_4$ , which crystallises from nitrobenzene in lustrous, bronze-green needles and forms a dihydrochloride which crystallises in lustrous, dark violet-red needles. R. H. P.

Formation of Rings from 1:8-Derivatives of Naphthalene. By EMILIO NOELTING (*Chem. Zeit.*, 1902, 26, 5).—1:8-Naphthylenedi-

amine readily yields iminoazoles. Thus, by the reduction of acetyl-1:8-nitronaphthylamine with stannous chloride and hydrochloric acid, the author obtained the iminoazole hydrochloride,  $\text{C}_{10}\text{H}_6\text{N}(\text{CMe})\text{NH}\cdot\text{HCl}$ .

This is a yellow, crystalline salt, rather sparingly soluble in cold, but readily in hot, water. It also dissolves readily in alcohol, but is insoluble in ether or benzene. The free base is precipitated by alkali hydroxide or by an acetate, but could not be obtained crystalline. When heated with phthalic anhydride and zinc chloride, it yields a yellow colouring matter. The corresponding phenyliminoazole is obtained by the reduction of benzoyl-1:8-nitronaphthylamine. It dyes silk and cotton, mordanted with tannin, yellow, although no tinctorial properties are possessed by the preceding methyl compound. With dimethyl-*p*-aminobenzaldehyde and protocatechuic aldehyde, 1:8-naphthylenediamine yields the dimethylamino- and the dihydroxy-derivatives of Ladenburg's aldehydin. Both these compounds have tinctorial properties.

A. F.

**Thio- and Seleno-antipyrines and the Constitution of Antipyrine.** By AUGUST MICHAELIS (*Annalen*, 1902, 320, 1—51).—The properties of antipyrine and its modes of formation are most easily ex-

plained on the assumption that it is a 2:5-pyrazole,  $\begin{array}{c} \text{CMe}=\text{NMe} \\ | \quad \text{O} < \\ \text{CH}=\text{C} \end{array} \text{NPh}$ ,

and not an isopyrazolone of the constitution  $\begin{array}{c} \text{CMe}\cdot\text{NMe} \\ | \quad \text{O} < \\ \text{CH}=\text{CO} \end{array} \text{NPh}$ . These two configurations are not very dissimilar; it is merely necessary to suppose that the oxygen atom is turned towards the interior of the ring so that it becomes influenced by the nitrogen atom in position 2. The imino-compound corresponding with 2:5-pyrazole formula has already been isolated (Michaelis and Gunkel, *Abstr.*, 1901, i, 351).

This view of the constitution of antipyrine derives considerable support from a study of the properties of its thio- and seleno-analogues.

[With H. BINDEWALD.]—Thioantipyrine (compare this vol., i, 120),

$\begin{array}{c} \text{CMe}=\text{NMe} \\ | \quad \text{S} < \\ \text{CH}=\text{C} \end{array} \text{NPh}$  (1-phenyl-2:3-dimethyl-2:5-thiopyrazole), develops

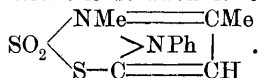
a transient, green coloration with ferric chloride, but not with nitrous acid; it is a less energetic antipyretic than antipyrine, but has no injurious after effects. Warm-blooded animals are not injured by subcutaneous and intravenous injections of the thio-compound; the nerves and mucous membrane are likewise unaffected. Thioantipyrine has a toxic action on the frog, whereas an equal dose of antipyrine is without effect.

Thioantipyrine hydrochloride,  $\begin{array}{c} \text{CMe}\cdot\text{NMeCl} \\ | \quad \text{CH}=\text{C}(\text{SH}) \end{array} \text{NPh}$ , separates in colourless crystals and melts at 128°; the *platinichloride*,

$(\text{C}_{11}\text{H}_{12}\text{N}_2\text{S})_2\cdot\text{H}_2\text{PtCl}_6\cdot 2\text{H}_2\text{O}$ , is a brownish-red precipitate melting and decomposing at 215°; the *sulphate*,  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{S}\cdot\text{H}_2\text{SO}_4$ , separates in colourless, cubical crystals. The

silver nitrate,  $\begin{array}{c} \text{CMe:NMe(NO}_3\text{)} \\ | \\ \text{CH}=\text{C(SAg)} \end{array} \text{>NPh}$ , crystallises in long, white needles melting at  $110^\circ$  and containing  $1\text{H}_2\text{O}$ , the corresponding *mercurichloride*,  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{S.HgCl}_2$ , is a white precipitate, the *aurichloride*,  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{S.HAuCl}_3$ , separates as a flesh-coloured precipitate.

The compound,  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{S.SO}_2$ , obtained as a yellow, crystalline precipitate on mixing aqueous solutions of thioantipyrine and sulphur dioxide, melts at  $89\text{--}91^\circ$ , and is reconverted into thioantipyrine when its alcoholic solution is evaporated; it probably has the constitution



*Thioantipyrine methiodide*,  $\begin{array}{c} \text{CMe:NMeI} \\ | \\ \text{CH:C(SMe)} \end{array} \text{>NPh}$ , produced by mixing

its generators, either alone or in alcoholic solution, crystallises from water in white needles with  $1\text{H}_2\text{O}$  and melts at  $90\text{--}92^\circ$ ; it separates from alcohol in anhydrous needles melting at  $192^\circ$ . When the methiodide is treated with a hot aqueous solution of sodium hydroxide, it is decomposed, yielding antipyrine, methyl mercaptan, and sodium iodide; silver oxide produces the same decomposition, but an unstable substituted ammonium hydroxide is formed as an intermediate product. *Thioantipyrine methochloride* is obtained either by neutralising the unstable hydroxide with hydrochloric acid or by treating the methiodide with silver chloride.

*Thioantipyrine benzoyl chloride*,  $\begin{array}{c} \text{CMe:NMeCl} \\ | \\ \text{CH}=\text{C(SBz)} \end{array} \text{>NPh}$ , prepared by mixing thioantipyrine and benzoyl chloride in benzene, crystallises from its chloroform solution on the addition of ether or benzene in white needles melting at  $100^\circ$ ; it is decomposed by an aqueous solution of alkali hydroxide, yielding thioantipyrine and the corresponding alkali chloride and benzoate.

*Thioantipyrine trioxide* (2-methylammonium-1-phenyl-3-methyl-2:5-pyrazolesulphonate),  $\text{SO}_2 \begin{array}{c} \text{NMe}=\text{CMe} \\ | \\ \text{O}-\text{C}=\text{CH} \end{array} \text{>NPh}$ , obtained by the action of oxidising agents on thioantipyrine, is readily prepared by the use of chlorine or bromine in aqueous solution; it crystallises either in white, silky needles or in well-defined, monoclinic prisms containing  $1\text{H}_2\text{O}$ . The hydrate loses its water at  $105^\circ$ , and melts indefinitely at  $288\text{--}290^\circ$ , evolving sulphur dioxide.

*Thioantipyrine dichloride* (2:5-dichloro-1-phenyl-2:3-dimethylthio-pyrazole),  $\begin{array}{c} \text{CMe:NMeCl} \\ | \\ \text{CH}=\text{C(SCl)} \end{array} \text{>NPh}$  or  $\begin{array}{c} \text{CMe}=\text{NMe} \\ | \quad | \\ \text{SCl}_2 < \quad < \\ \text{CH}=\text{C} \end{array} \text{>NPh}$ , produced

by the action of dry chlorine on a chloroform solution of thioantipyrine, crystallises in unstable, yellow needles the aqueous solution of which yields on dilution a yellow oil having the composition  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{SCl.OH}$ ; the latter derivative, on further decomposition with sodium hydroxide solution, furnishes thioantipyrine. The corresponding *bromide* melts at  $154^\circ$ , and on treatment with water yields an oily hydroxy-bromide.

*Bromothioantipyrine* (4-bromo-1-phenyl-2:3-dimethyl-2:5-thiopyrazole),  

$$\begin{array}{c} \text{CMe}=\text{N} \\ | \quad \text{S} < \\ \text{CBr}=\text{C} \end{array} \text{NPh}$$
, readily obtained from 5-chloro-4-bromo-1-phenyl-3-methylpyrazole methiodide, crystallises from alcohol in prisms and from water in white needles and melts at 188°; the methiodide itself, produced from 5-chloro-4-bromo-1-phenyl-3-methylpyrazole by the action of methyl iodide, forms white leaflets melting at 230°.

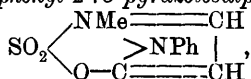
When heated, antipyrine methiodide loses methyl iodide and regenerates the original base; thioantipyrine methiodide, on the other hand, yields 1-phenyl-3-methyl-5-thiomethylpyrazole,  

$$\begin{array}{c} \text{CMe}:\text{N} \text{---} \\ | \quad \text{CH}:\text{C}(\text{SMe}) \end{array} \text{NPh}$$
, the elimination of alkyl iodide taking place at 210–220°; the product, a colourless oil rapidly becoming yellow, boils at 196–198° under 30 mm. pressure and recombines with methyl iodide only at 100–110°, giving rise to the original methiodide.

1-Phenyl-2-methyl-2:5-thiopyrazole,  

$$\begin{array}{c} \text{CH}=\text{NMe} \\ | \quad \text{S} < \\ \text{CH}=\text{C} \end{array} \text{NPh}$$
, obtained by the action of potassium hydrosulphide on 5-chloro-1-phenylpyrazole methiodide (m. p. 172°) crystallises in needles and melts at 162°; the *platinichloride*,  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{S}_2\text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$ , is an orange-yellow precipitate; the *mercurichloride*,  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{S}_2\text{HgCl}_2$ , and *ferrocyanide*,  $(\text{C}_{10}\text{H}_{10}\text{N}_2\text{S})_2\text{H}_2\text{FeCy}_6$ , are white, insoluble substances, the former melting at 220°; the *methiodide* melts at 156°.

2-Methylammonium-1-phenyl-2:5-pyrazolesulphonate,

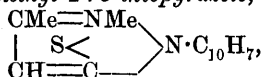


produced by the action of chlorine on an aqueous solution of 1-phenyl-2-methyl-2:5-thiopyrazole, separates in transparent, monoclinic crystals.

*Methylthioantipyrine* (1-phenyl-2:3:4-trimethyl-2:5-thiopyrazole),  

$$\begin{array}{c} \text{CMe}=\text{NMe} \\ | \quad \text{S} < \\ \text{CMe}=\text{C} \end{array} \text{NPh}$$
, prepared from 5-chloro-1-phenyl-3:4-dimethylpyrazole methiodide (compare Abstr., 1901, i, 407) forms white crystals melting at 129°.

1-β-Naphthyl-2:3-dimethyl-2:5-thiopyrazole,



and 1-β-naphthyl-2:3:4-trimethyl-2:5-thiopyrazole melt respectively at 135° and 169°.

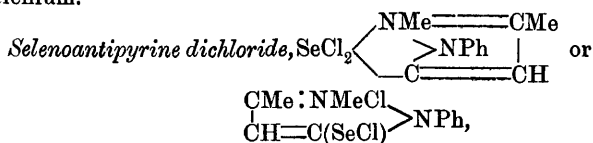
[With M. STEIN.]—*Selenoantipyrine* (1-phenyl-2:3-dimethyl-2:5-selenopyrazole),  

$$\begin{array}{c} \text{CMe}=\text{NMe} \\ | \quad \text{Se} < \\ \text{CH}=\text{C} \end{array} \text{NPh}$$
, obtained by the action of hydrogen

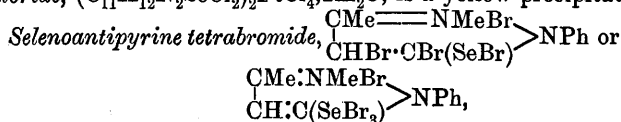
selenide on a suspension of antipyrine in potassium hydroxide solution, separates from water, alcohol, or chloroform in lustrous, pale yellow crystals and melts at 168°; it does not develop a coloration

with ferric chloride, and only gives a faint green colour with nitrous acid. The hydrochloride and sulphate do not crystallise; the *platini-chloride*,  $(C_{11}H_{12}N_2Se)_2 \cdot H_2PtCl_6$ , is a pulverulent, brownish-yellow precipitate; the *mercurichloride*,  $C_{11}H_{12}N_2Se \cdot HgCl_2$ , and *ferrocyanide*,  $(C_{11}H_{12}N_2Se)_2 \cdot H_4Fe(CN)_6$ , are white, insoluble substances, the former melting at  $240^\circ$ . *Selenoantipyrine methiodide*,  $\begin{array}{c} CMe=NMeI \\ | \\ CH:C(SeMe) \end{array} > NPh$ , obtained from its generators at the ordinary temperature, separates from water in needles and melts at  $197^\circ$ ; the *ethiodide* melts at  $152^\circ$ ; these alkyl iodides, when treated with potassium hydroxide solution, are decomposed, yielding antipyrine, potassium iodide, and the corresponding selenomercaptan.

*Selenoantipyrine trioxide* (2-methylammonium-1-phenyl-3-methyl-2:5-pyrazoleselenonate),  $SeO_2 \begin{array}{c} NMe=CM \\ | \\ O \cdot C > NPh \\ | \\ CH \end{array}$ , produced by oxidising selenoantipyrine with aqueous chlorine solution and freeing the initial product of reaction from the hydroxychloride,  $C_{11}H_{12}N_2ClSe \cdot OH$ , by repeated crystallisation from alcohol, separates from this solvent in needles with  $1H_2O$ , and decomposes at  $170^\circ$  with the elimination of selenium.



prepared either by heating the trioxide with concentrated hydrochloric acid or by passing chlorine into a chloroform solution, crystallises from glacial acetic acid or alcohol in yellow needles; its *platini-chloride*,  $(C_{11}H_{12}N_2SeCl_2)_2 \cdot PtCl_4 \cdot 2H_2O$ , is a yellow precipitate.



produced by adding bromine to a chloroform solution of selenoantipyrine, crystallises in lustrous, yellow needles and melts at  $139^\circ$ .

*Selenoantipyrine dibromide*,  $C_{11}H_{12}N_2Br_2Se$ , results from the action of hydrogen bromide on selenoantipyrine trioxide, and is also produced on evaporating the aqueous solution of the tetrabromide; it forms orange-red needles and melts at  $236^\circ$ ; the *diiodide*,  $C_{11}H_{12}N_2I_2Se$ , separates from alcohol or chloroform in brown crystals and melts at  $144^\circ$ .

*4-Methylselenoantipyrine* (1-phenyl-2:3:4-trimethyl-2:5-selenopyrazole),  $\begin{array}{c} CMe=NMe \\ | \\ Se < \\ | \\ CMe=C \end{array} > NPh$ , obtained from 5-chloro-1-phenyl-3:4-dimethylpyrazole methiodide by the action of potassium hydroselenide in alcoholic solution, crystallises in slender, yellow needles and melts at  $172^\circ$ ; it forms a trioxide and a *dichloride*,  $C_{12}H_{14}N_2Cl_2Se$  (m. p.  $207-208^\circ$ ).

G. T. M.



**Derivatives of 1:2-Pyrone or Coumalin from Pyrazolines.** By EDUARD BUCHNER and HEINRICH SCHRÖDER (*Ber.*, 1902, **35**, 782—790. Compare *Abstr.*, 1895, i, 250).—

*Methyl 5-acetyl-4-phenylpyrazoline-3:5-dicarboxylate*,  $\text{CO}_2\text{Me}\cdot\text{C}\cdot\text{Ac} \begin{smallmatrix} \text{CHPh}\cdot\text{C}\cdot\text{CO}_2\text{Me} \\ \text{NH}-\text{N} \end{smallmatrix}$ , is pre-

pared when mol. proportions of methyl benzylideneacetoacetate and methyl diazoacetate are heated together for 4 days at 45—60°, and forms crystals melting at 103°; the *phenylhydrazone*,  $\text{C}_{21}\text{H}_{22}\text{O}_4\text{N}_4$ , is a yellow, crystalline powder melting and decomposing at 155—157°. When the corresponding ethyl ester is treated with bromine in chloroform solution, ethyl 4-phenylpyrazole-3:5-dicarboxylate (m. p. 96°) is formed (this vol., i, 236).

*Ethyl 4-phenyl-6-methyl-1:2-pyrone-5-carboxylate*,



is obtained when ethyl 5-acetyl-4-phenylpyrazolinedicarboxylate is gradually heated from 160° to 230° in carbon dioxide, and the product fractionated under reduced pressure; it crystallises in colourless, lustrous needles melting at 104°. When boiled with aqueous sodium hydroxide,  $\beta$ -phenylglutaconic acid (m. p. 154°) is formed, together with acetic acid.  $\beta$ -Phenylglutaconic anhydride is obtained when  $\beta$ -phenylglutaconic acid is heated with acetyl chloride, and crystallises in lustrous leaflets decomposing at 197—199°.

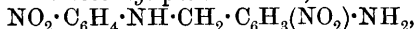
*Ethyl 3-bromo-4-phenyl-6-methyl-1:2-pyrone-5-carboxylate*,



prepared by the action of bromine on ethyl phenylmethyl-1:2-pyrone-carboxylate, crystallises in long, colourless needles melting at 72°. By the action of concentrated potassium hydroxide, it is converted into 3-phenyl-5-methylfurfuran-2:4-dicarboxylic acid,  $\text{C}_4\text{OPhMe}(\text{CO}_2\text{H})_2$ , which crystallises in colourless needles melting and decomposing at 224°. On boiling the brominated ester with 40 per cent. potassium hydroxide, 3-phenyl-5-methylfurfuran is obtained, crystallising in colourless, hair-like needles melting at 80—81°.

*Methyl 4-methyl-5-acetylpyrazoline-3:5-dicarboxylate* was prepared from methyl ethylideneacetoacetate and methyl diazoacetate, and formed colourless crystals melting at 85°. When heated, it is converted into methyl 4:6-dimethyl-1:2-pyrone-5-carboxylate (m. p. 67°). By the action of bromine, the latter is brominated, yielding *methyl 3-bromo-4:6-dimethyl-1:2-pyrone-5-carboxylate*, which crystallises in long, colourless needles melting at 135°. K. J. P. O.

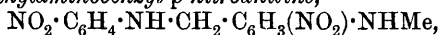
**Action of Formaldehyde on *p*-Nitroaniline.** By JACOB MEYER and OTTO STILLICH (*Ber.*, 1902, **35**, 739—746. Compare *Abstr.*, 1900, i, 222).—5-Nitro-2-aminobenzyl-*p*-nitroaniline,



prepared by treating a solution of *p*-nitroaniline in concentrated acetic and sulphuric acids with 40 per cent. formaldehyde solution, crystallises from acetone or glacial acetic acid in oblique prisms melting at 227—228°. Its *monoacetyl* derivative, obtained by warming the base with acetic anhydride and sulphuric acid, crystallises in long, yellow

needles and melts at 241—242°; it is accompanied by another substance melting at 280°, which, when heated with water, evolves acetic acid and yields the monoacetyl compound. *Diacetyl-5-nitro-2-aminobenzyl-p-nitroaniline*, produced by boiling the base with 4 parts of acetic anhydride, separates from alcohol in white, crystalline aggregates and melts at 210—211°.

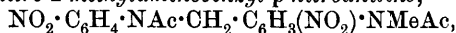
*5-Nitro-2-methylaminobenzyl-p-nitroaniline*,



a bye-product in the preceding formaldehyde condensation, crystallises from acetone or glacial acetic acid.

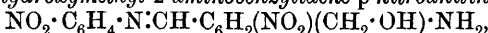
The two substituted benzyl-*p*-nitroanilines are hydrolysed by 40 per cent. sulphuric acid, yielding *p*-nitroaniline, but the methylated base is only partially decomposed.

*Diacetyl-5-nitro-2-methylaminobenzyl-p-nitroaniline*,



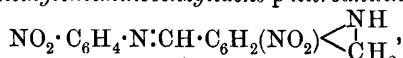
crystallises from ethyl acetate in prismatic needles and melts at 216—218°; this substance does not evolve hydrogen when treated with sodium in toluene, and hence it is concluded that the parent base has the constitution indicated.

*5-Nitro-3-hydroxymethyl-2-aminobenzylidene-p-nitroaniline*,



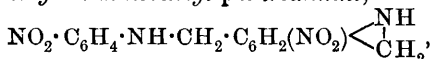
is also produced in the condensation between formaldehyde and *p*-nitroaniline in glacial acetic acid; it crystallises from alcohol in yellow, right-angled prisms and melts at 207—208°; the *monoacetyl* derivative, obtained by heating the base for 30 minutes with acetic anhydride, crystallises from alcohol in white needles and melts and decomposes at 223—225°. This benzylidene derivative is hydrolysed even by 8 per cent. sulphuric acid.

*5-Nitro-3 : 2-methyleneiminobenzylidene-p-nitroaniline*,



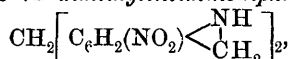
produced by boiling the hydroxy-methyl base with glacial acetic acid, crystallises from acetone in heavy, golden-yellow plates and melts at 243—246°; it does not react with acetic anhydride even on prolonged heating.

*5-Nitro-3 : 2-methyleneiminobenzyl-p-nitroaniline*,



produced by condensing *p*-nitroaniline and formaldehyde in glacial acetic acid containing half its weight of concentrated sulphuric acid, was, however, only obtained in one experiment; it separates in acicular aggregates and melts at 219—222°.

*5 : 5'-Dinitro-3 : 2 : 3' : 2'-dimethyleneiminodiphenylmethane*,



prepared by heating *p*-nitroaniline and formaldehyde with concentrated hydrochloric acid and saturating the mixture with hydrogen chloride, crystallises from glacial acetic acid in needles and melts at 250—251°; its acetyl derivative is insoluble.

G. T. M.

**Derivatives of Triazan.** IV. By HUGO VOSWINCKEL (*Ber.*, 1902, 35, 689).—The compounds,  $C_8H_9ON_3$ ,  $C_8H_{11}ON_3$ ,  $C_{15}H_{14}O_2N_4$ ,  $C_8H_8ON_3Cl$ , and  $C_8H_{10}ON_2Cl$ , of Bamberger, Grob, and Free (this vol., i, 246, 247, 248) are identical with substances already described by the author (*Abstr.*, 1899, i, 958; 1901, i, 53, 617), although formulated differently.

T. M. L.

**Voswinckel's Triazan Derivatives.** By EUGEN BAMBERGER (*Ber.*, 1902, 35, 756—759. See preceding abstract).—The author shows that the triazan derivatives described by Voswinckel (*Abstr.*, 1899, i, 958) are identical with phenylazoacetaldoxime and its derivatives described by himself and Grob (this vol., i, 247). The author claims that his interpretation of the constitution of these compounds is correct.

R. H. P.

**Triazan Derivatives.** By HUGO VOSWINCKEL (*Ber.*, 1902, 35, 1009—1012).—The author admits that the formulæ given by Bamberger (preceding abstract) for the substances originally prepared by himself are probably more correct than those first suggested (*Abstr.*, 1899, i, 958). The ring formulæ for the reduction products are, however, still retained.

J. J. S.

**Formula of Triazole.** I. and II. By GUIDO PELLIZZARI (*Atti R. Accad. Lincei*, 1901, [v], 10, ii, 297—303; and 1902, [v], 11, i, 20—23).—The four possible triazoles may be classified in two pairs, the two members of each pair corresponding with one and the same nucleus. In the present communication, the author deals

with 1:2:4-triazole,  $NH \begin{smallmatrix} N=CH \\ | \\ CH:N \end{smallmatrix}$ , and 1:3:4-triazole,  $NH \begin{smallmatrix} CH:N \\ | \\ CH:N \end{smallmatrix}$

which he considers to be identical compounds. The substance known as 1:2:4-triazole has been obtained by the following six methods, of which only the first two point to the 1:2:4-constitution, whilst the others are explained equally well by the 1:2:4- or the 1:3:4-formula. (1) Oxidation of 1-phenyl-1:2:4-triazole by means of acid potassium permanganate. (2) Heating of 1:2:4-triazolecarboxylic acid. (3) Reduction of urazole by means of phosphorus pentasulphide. (4) Action of formamide on formylhydrazide. (5) From thiosemicarbazide. (6) Action of nitrous acid on tetrazoline. The author finds that the product obtained by oxidising 1-phenyl-1:3:4-triazole with potassium permanganate in acid solution is identical with that obtained from 1-phenyl-1:2:4-triazole. The two triazoles, 1:2:4- and 1:3:4-, are

hence represented by the formula 
$$\begin{array}{c} N \cdots N \\ | \quad | \\ HC \cdot H \cdot CH \\ \diagdown \quad \diagup \\ N \end{array}$$
 in which the positions

of the double linkings will depend on where the iminic hydrogen is situated.

T. H. P.

**Constitution of Phenylurazole.** By MAX BUSCH (*Ber.*, 1902, 35, 971—972).—A claim for priority (compare Acree, this vol., i, 242).

R. H. P.

**Molecular Transformation in the Urazole Series.** By MAX BUSCH (*Ber.*, 1902, 35, 973—976).—When heated at 220—221°, the

compound  $\text{NPh} \begin{array}{c} \text{C}(\text{SH}) \cdot \text{NPh} \\ \diagup \quad \diagdown \\ \text{O} \\ \diagdown \quad \diagup \\ \text{C} = \text{N} \end{array}$  (Abstr., 1901, i, 235) is transformed

into 1:4-diphenyl-5-thiourazole. Various analogous compounds, previously described (*loc. cit.*), undergo similar transformations.

R. H. P.

*p*-Diketohexahydrotetrazine and *p*-Diketothiohexahydrotetrazine. II. By ATTILIO PURGOTTI and G. VIGANÒ (*Gazzetta*, 1901, 31, ii, 550—566. Compare Abstr., 1897, i, 640).—Attempts to prepare 1:2:4:5-tetrazine from *p*-urazine by reduction with phosphorus pentasulphide have as yet proved unsuccessful.

The action of hydrazodicarbonamide on phenylhydrazine yields phenylurazole in large quantity, and possibly also phenyl-*p*-urazine, but the latter could not be separated in a pure condition.

*Diacetyl-p*-urazine,  $\begin{array}{c} \text{NH} \cdot \text{CO} \cdot \text{N} \cdot \text{Ac} \\ | \quad | \\ \text{NH} \cdot \text{CO} \cdot \text{N} \cdot \text{Ac} \end{array}$ , is obtained as a thick, yellow syrup, soluble in water but insoluble in alcohol or ether; on evaporating its solution, it yields the corresponding *monoacetyl* derivative,  $\text{C}_4\text{H}_6\text{O}_3\text{N}_4$ , separating in small, white scales which decompose without melting at 235°, and are soluble in water, alcohol, or ether.

With methyl iodide, *p*-urazine forms a dimethiodide,  $\text{C}_2\text{H}_4\text{O}_2\text{N}_2 \cdot 2\text{MeI}$ , which separates from water in white plates dissolving slightly in alcohol or ether and decomposing at 200°.

*p*-Urazine (1 mol.) reacts with aldehydes (1 mol.), and with either 1 or 2 mols. of ketones.

*Salicylidene-p*-urazine,  $\begin{array}{c} \text{NH} \cdot \text{CO} \cdot \text{N} \\ | \quad | \\ \text{NH} \cdot \text{CO} \cdot \text{N} \end{array} > \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , is deposited from alcohol in white, shining leaflets which melt at 219° and dissolve slightly in ether, but are insoluble in water.

*m*-Nitrobenzylidene-*p*-urazine,  $\begin{array}{c} \text{NH} \cdot \text{CO} \cdot \text{N} \\ | \quad | \\ \text{NH} \cdot \text{CO} \cdot \text{N} \end{array} > \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , forms minute crystals soluble in ether, but insoluble in water or alcohol.

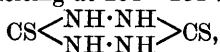
$\beta$ -Propylidene-*p*-urazine,  $\begin{array}{c} \text{NH} \cdot \text{CO} \cdot \text{N} \\ | \quad | \\ \text{NH} \cdot \text{CO} \cdot \text{N} \end{array} > \text{CMe}_2$ , separates in small, white scales, which melt at 203—204°, giving a yellow liquid, and are soluble in water or alcohol but almost insoluble in ether or acetic acid.

*Dibenzophenone-p*-urazine,  $\text{CPh}_2 < \begin{array}{c} \text{N} \cdot \text{CO} \cdot \text{N} \\ | \quad | \\ \text{N} \cdot \text{CO} \cdot \text{N} \end{array} > \text{CPh}_2$ , crystallises from ether in pale yellow, monoclinic scales [ $a:b:c = 4.0054:1:2.9889$ ;  $\beta = 85^\circ 29\frac{1}{2}'$ ], which melt at 164° and are soluble in acetic acid.

*Diacetophenone-p*-urazine,  $\text{CPhMe} < \begin{array}{c} \text{N} \cdot \text{CO} \cdot \text{N} \\ | \quad | \\ \text{N} \cdot \text{CO} \cdot \text{N} \end{array} > \text{CPhMe}$ , separates from alcohol in yellow, monoclinic crystals [ $a:b:c = 1.3310:1:1.1675$ ;  $\beta = 76^\circ 17'$ ], which melt at 124° and are soluble in ether, acetone, chloroform, or acetic acid.

*Dithio-p*-urazine hydrochloride,  $\text{C}_2\text{H}_4\text{N}_4\text{S}_2 \cdot \text{HCl}$ , prepared by boiling

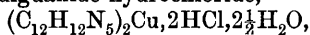
dithiohydrazodicarbonamide with alcoholic hydrazine hydrate and precipitating the product with hydrochloric acid, crystallises from water in white, shining needles melting at 231—232°. *Dithio-p-urazine*,



obtained from the hydrochloride by the action of barium hydroxide, separates in small, white crystals melting at 198—199°; it has a faint alkaline reaction, dissolves readily in water and to a slight extent in alcohol, and reacts with aldehydes. The silver salt,  $\text{C}_2\text{H}_3\text{N}_4\text{S}_2\text{Ag}$ , crystallises from water in white leaflets. *Benzylidenethio-p-urazine* separates from alcohol in yellow crystals which melt at 215° and decompose at 220°. *Salicylidenedithio-p-urazine* forms yellow crystals melting and decomposing at 226°. T. H. P.

**$\alpha$ - and  $\beta$ -Naphthyldiguanide.** By ALOIS SMOLKA and ED. HALLA (*Monatsh.*, 1901, **22**, 1146—1164. Compare Abstr., 1889, 951).— *$\alpha$ -Naphthyldiguanide*, formed from dicyanodiamide and  $\alpha$ -naphthylamine hydrochloride, crystallises from dilute alcohol in nacreous leaflets which contain  $\frac{1}{2}\text{H}_2\text{O}$  and melt at 158°. The following salts have been prepared: the *monohydrochloride*,  $\text{C}_{12}\text{H}_{13}\text{N}_5\text{HCl}$ , which crystallises from dilute alcohol in white needles; the *dihydrochloride*,  $\text{C}_{12}\text{H}_{13}\text{N}_5 \cdot 2\text{HCl}$ , formed by boiling the monohydrochloride with hydrochloric acid; the *mononitrate*,  $\text{C}_{12}\text{H}_{13}\text{N}_5\text{HNO}_3$ , delicate needles from water; the *mono-sulphate*,  $(\text{C}_{12}\text{H}_{13}\text{N}_5)_2\text{H}_2\text{SO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , which loses its water at 120°; the *platinichloride*,  $\text{C}_{12}\text{H}_{13}\text{N}_5\text{H}_2\text{PtCl}_6$ , precipitated by addition of hydrochloric acid and platinum chloride to the monohydrochloride. The copper compounds of  $\alpha$ -naphthyldiguanide are rose-red, but in the anhydrous state violet. Being only slightly soluble in hot alcohol and less so in water, they do not crystallise easily. On prolonged boiling with water they become brown and are partially decomposed. Copper  $\alpha$ -naphthyldiguanide,  $(\text{C}_{12}\text{H}_{12}\text{N}_5)_2\text{Cu} \cdot 2\text{H}_2\text{O}$ , is precipitated from a solution of the monohydrochloride and copper sulphate on addition of sodium hydroxide.

Copper- $\alpha$ -naphthyldiguanide hydrochloride,



is formed by addition of an alcoholic solution of the diguanide to an aqueous solution of cupric chloride. The salt separates in crusts on spontaneous evaporation of the solution. Copper- $\alpha$ -naphthyldiguanide nitrate,  $(\text{C}_{12}\text{H}_{12}\text{N}_5)_2\text{Cu} \cdot 2\text{HNO}_3$ , is precipitated by addition of cupric nitrate solution to an alcoholic solution of the diguanide. Copper- $\alpha$ -naphthyldiguanide sulphate  $(\text{C}_{12}\text{H}_{12}\text{N}_5)_2\text{Cu} \cdot \text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , is precipitated by addition of sodium sulphate to a dilute alcoholic solution of the diguanide copper hydrochloride.

*$\beta$ -Naphthyldiguanide* and its derivatives are prepared by the same methods; they are more stable and crystallise more easily than the corresponding  $\alpha$ -compounds.  $\beta$ -Naphthyldiguanide crystallises from boiling water in thin, glistening leaflets which melt at 180° with evolution of gas. The following salts have been prepared: the *monohydrochloride*; the *mononitrate*; the *mono- and di-sulphates*,  $(\text{C}_{12}\text{H}_{13}\text{N}_5)_2\text{H}_2\text{SO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  and  $\text{C}_{12}\text{H}_{13}\text{N}_5\text{H}_2\text{SO}_4$ ; the *platinichloride*.

Copper- $\beta$ -naphthyldiguanide is precipitated from the solution of its

hydrochloride by addition of sodium hydroxide. The hydrochloride,  $(C_{12}H_{12}N_5)_2Cu, 2HCl, 2H_2O$ ; the nitrate,  $(C_{12}H_{12}N_5)_2Cu, 2HNO_3$ ; and the sulphate,  $(C_{12}H_{12}N_5)_2Cu, H_2SO_4, 1\frac{1}{2}H_2O$ , have been prepared.

With nickel salts,  $\beta$ -naphthyldiguanide forms slightly soluble, yellow compounds. G. Y.

**Alkylation of Phenylazoacetaldoxime.** By EUGEN BAMBERGER and JOHANNES FREI (*Ber.*, 1902, 35, 746—756. See this vol., i, 247).—When treated with methyl iodide and sodium methoxide, phenylazoacetaldoxime yields 1-phenyl-3-methyltriazole. The *N*-methyl ether of the oxime,  $NPh:N \cdot CMe \begin{smallmatrix} O \\ \diagup \\ NMe \end{smallmatrix}$ , obtained by the action of diazomethane on the oxime, or of methyl iodide on its sodium derivative, crystallises in long, silky, orange needles from water, melts at  $96-96.5^\circ$ , and has no odour; when heated with sodium methoxide, it yields 1-phenyl-3-methyltriazole, and, when reduced, a mixture of aniline and phenylhydrazine. The *O*-methyl ether,  $NPh:N \cdot CMe:N \cdot OMe$ , obtained by the action of methyl iodide on the silver salt, is an orange-coloured oil, which solidifies at the temperature of a mixture of ice and salt, boils at  $133-134^\circ$  under 12 mm. pressure, is insoluble in water, and has a very characteristic sweet odour.

When the *O*-methyl ether is treated with concentrated hydrochloric acid, it yields the hydrochloride of *p*-chlorophenylhydrazoacetaldoxime methyl ether, which crystallises in glistening, yellowish-white leaflets; this, when treated with potassium acetate, forms *p*-chlorophenylazoacetaldoxime methyl ether, which crystallises in slender, golden, silky needles melting at  $75.5-76^\circ$ .

The *O*-ethyl ether of the oxime crystallises in orange-yellow, lustrous leaflets, melts at  $39-39.5^\circ$ , and has a characteristic odour; the isopropyl ether is a bright red oil; both these ethers react with hydrochloric acid in a manner similar to the methyl ether. R. H. P.

**Quinonoid Diazo-compounds and the so-called Triazolens.** By ARTHUR HANTZSCH (*Ber.*, 1902, 35, 888—896).—The diazo-compound from *p*-aminodiphenylamine (Ikuta, *Abstr.*, 1888, 467; Jacobson, *Abstr.*, 1896, i, 23) resembles the aniline derivatives in that it forms a neutral diazonium chloride. It gives a yellow potassium anilino-benzeneazosulphonate,  $NHPh \cdot C_6H_4 \cdot N_2 \cdot SO_3K$ , with potassium hydrogen sulphite in the normal way; the silver salt is a dark red precipitate; the acid crystallises in glistening red prisms and forms a hydrochloride,  $C_{12}H_{11}N_3SO_3 \cdot HCl$ ; the phenylsulphone,  $NHPh \cdot C_6H_4 \cdot N_2 \cdot SO_2Ph$ , from the diazonium sulphate and sodium benzenesulphonate forms red crystals, melts at  $82^\circ$ , and does not dissolve in water, but is soluble in organic solvents. The action of potassium cyanide also proceeds normally, giving an anilino-benzeneazocyanide,  $NHPh \cdot C_6H_4 \cdot N:N \cdot CN$ , which forms a carmine-red powder, melts at  $129^\circ$ , and does not dissolve in water but dissolves in organic solvents. The action of potassium hydroxide gives rise to a compound which is regarded as phenylimino-quinone diazide,  $NPh \cdot C_6H_4 \cdot \begin{smallmatrix} N \\ \diagup \\ N \end{smallmatrix}$ ; it forms a grey-brown powder and

very readily decomposes. This type of diazo-compound has only been known hitherto in the so-called diazophenols,  $O:C_6H_4:N_2$  (Wolff, *Annalen*, 1900, 312, 126), of which the above compound would be the phenylimino-derivative, but a similar constitution,  $N \begin{smallmatrix} \diagup C_6H_4 \\ \diagdown N \end{smallmatrix} > C \begin{smallmatrix} N \\ | \\ N \end{smallmatrix}$ , is now suggested for the triazolens.

The *diazochloride* of dimethyl-*p*-phenylenediamine was also prepared, but could not be converted into a compound of the above type; mono-methyl-*p*-phenylenediamine could not be converted into a diazo-compound, as nitrogen was vigorously given off even below  $0^\circ$ .

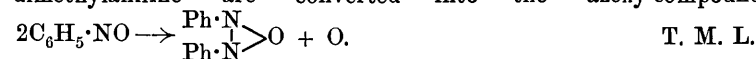
T. M. L.

**Azotates of the Fatty Series.** By ARTHUR HANTZSCH and MARTIN LEHMANN (*Ber.*, 1902, 35, 897—905).—*Potassium methylazotate*,  $CH_3 \cdot N:N \cdot OK, H_2O$ , the first metallic diazotate which has been isolated in the fatty series, separates in white scales on shaking nitrosomethylurethane with concentrated aqueous potassium hydroxide; it is very unstable in presence of moisture, and on heating decomposes partially into diazomethane and potassium hydroxide; a similar decomposition occurs with explosive violence on adding a drop of water to a mass of the salt. The *rubidium* and *sodium* salts are similarly constituted, but are less readily purified. The *alcoholate*,  $CH_3 \cdot N:N \cdot OK, EtOH$ , is formed as a white precipitate by the action of potassium ethoxide on ethereal nitrosomethylurethane.

*Potassium benzylazotate*,  $CH_2Ph \cdot N:N \cdot OK, H_2O$ , is a white salt, but rapidly turns reddish owing to partial decomposition. The *alcoholate*,  $CH_2Ph \cdot N:N \cdot OK, EtOH$ , forms a white, crystalline powder, and when moistened with water decomposes into benzyl ethyl ether and stilbene.

*Phenyldiazomethane*,  $CHPh \begin{smallmatrix} N \\ | \\ N \end{smallmatrix}$ , which Pechmann was not able to isolate, was obtained as a reddish-brown oil by cautiously warming nitrosobenzylmethane with concentrated potassium hydroxide. When distilled, it loses nitrogen and is converted into stilbene; with water, it gives benzyl alcohol, and with alcohol benzyl ethyl ether.

When treated in a similar manner, nitrosobenzene and nitroso-dimethylaniline are converted into the azoxy-compounds,



**Action of Diazo-compounds on the Esters of 2-Acyl-1:3-ketonic Acids.** By CARL BÜLOW and EKKEHARD HAILER (*Ber.*, 1902, 35, 915—938).—By the action of diazobenzene chloride on ethyl diacetylacetate or acetylpropionylacetate, an acetyl or propionyl group is eliminated, and an ethyl phenylazoacetoacetate is produced identical with that prepared from diazobenzene chloride and ethyl acetoacetate. The *acetyl* derivative,  $NPhAc \cdot N:CAc \cdot CO_2Et$ , prepared by warming the azo-compound with zinc chloride and acetic anhydride, crystallises from alcohol in colourless prisms, melts at  $119-120^\circ$ , and gives acetanilide when reduced with zinc dust and dilute sulphuric acid.

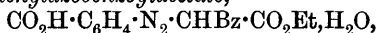
Ethyl phenyleneazobenzoylacetate is formed by loss of an acetyl

group when ethyl acetylbenzoylacetate is treated with diazobenzene chloride. The *amide*,  $\text{NPh}\cdot\text{N}:\text{CBz}\cdot\text{CO}\cdot\text{NH}_2$ , crystallises from alcohol in yellow flakes or needles and melts at  $163-165^\circ$ . 4-Hydroxy-5-benzeneazo-2 : 6-diphenyl-1 : 3-diazine,  $\text{N}_2\text{Ph}\cdot\text{C}\begin{smallmatrix} \text{CPh}=\text{N} \\ \text{C}(\text{OH})\cdot\text{N} \end{smallmatrix}$  CPh, prepared from the azo-ester and benzamidine hydrochloride, crystallises from alcohol in long, golden-yellow, glistening needles and melts at  $138-139^\circ$ . The *acetyl* derivative of the azo-ester,  $\text{NAcPh}\cdot\text{N}:\text{CBz}\cdot\text{CO}_2\text{Et}$ , crystallises from alcohol in rosettes of minute, white, silky needles, melts at  $151^\circ$ , and yields acetanilide when reduced.

Ethyl *o*-tolylazobenzoylacetate,  $\text{C}_7\text{H}_7\cdot\text{N}_2\cdot\text{CHBz}\cdot\text{CO}_2\text{Et}$ , prepared by the action of *o*-diazotoluene chloride on ethyl benzoylacetate or ethyl acetylbenzoylacetate, crystallises from alcohol in yellowish-red prisms and melts at  $86^\circ$ . A similar displacement of the acetyl group occurs in the interaction of *p*-nitrodiazobenzene chloride with ethyl acetylbenzoylacetate (compare Stierlin, Abstr., 1888, 1088 and 1298).

Ethyl diphenylbisazobenzoylacetate,  $\text{C}_{12}\text{H}_8(\text{N}_2\cdot\text{CHBz}\cdot\text{CO}_2\text{Et})_2$ , from diazotised benzidine and ethyl acetylbenzoylacetate, separates as a yellow powder, but crystallises from acetic acid in stout, red prisms; the yellow modification becomes red at  $180^\circ$ , and both forms melt at  $187^\circ$ . It condenses with phenylhydrazine to a compound,  $\text{C}_{38}\text{H}_{30}\text{O}_4\text{N}_6$ , in which one of the acetoacetate groups is converted in the normal way into a pyrazolone; this separates in small, red crystals from the acetic acid solution and melts at  $215^\circ$ .

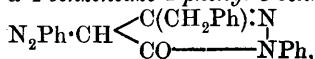
Ethyl carboxyphenylazobenzoylacetate,



from *o*-diazobenzoic acid and ethyl acetylbenzoylacetate, crystallises from alcohol in yellow needles and melts at  $145-147^\circ$ ; the ammonium salt forms yellow flakes; the sodium and silver salts form hair-like, yellow needles. The acid,  $\text{C}_{16}\text{H}_{12}\text{O}_5\text{N}_2$ , obtained on hydrolysing the ester, is a yellow substance and melts at  $220^\circ$ . 4-Carboxybenzeneazo-1 : 3-diphenylpyrazolone,  $\text{C}_{22}\text{H}_{16}\text{O}_3\text{N}$ , prepared by the action of phenylhydrazine on the ester, crystallises from acetic acid in hair-like, felted needles and melts at  $276^\circ$ . 4-Carboxybenzeneazo-3-phenyl-5-isooxazolone, prepared by the action of hydroxylamine hydrochloride on the ester, separates from acetic acid in yellow needles and melts at  $245-250^\circ$ .

4-Sulphobenzeneazo-1 : 3-diphenylpyrazolone,  $\text{C}_{21}\text{H}_{16}\text{O}_4\text{N}_4\text{S}$ , prepared by the action of phenylhydrazine on the product from diazotised sulphanilic acid and ethylacetylbenzoylacetate, forms dark red prisms or needles and melts and decomposes at  $275^\circ$ .

Ethyl acetylphenylacetylacetate,  $\text{CH}_3\text{Ph}\cdot\text{CO}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$ , prepared in an impure state by Fischer and Bülow (Abstr., 1885, 1237), is a yellowish liquid and boils with partial decomposition at  $190^\circ$  under 15 mm. pressure; the copper salt,  $(\text{C}_{14}\text{H}_{15}\text{O}_4)_2\text{Cu}$ , forms slender, blue, silky needles and melts at  $182-183^\circ$  to a brown liquid, dissolves readily in chloroform or in hot benzene, and crystallises from alcohol. When condensed with diazobenzene chloride and then with phenylhydrazine, it gives a 4-benzeneazo-1-phenyl-3-benzylpyrazolone,





which crystallises from acetic acid in yellowish-red needles and melts at 147°.

*Ethyl phenylazoacetyl-p-nitrobenzoylacetate*,



from diazobenzene chloride and ethyl acetyl-p-nitrobenzoylacetate, crystallises from alcohol in yellow flakes and melts and decomposes at 126—127°.

*Ethyl acetyl-m-nitrobenzoylacetate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CHAc} \cdot \text{CO}_2\text{Et}$ , crystallises from alcohol in stout, yellowish prisms and melts at 74—75°.

*Ethyl m-nitrobenzoylacetate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , crystallises from alcohol in reddish-white prisms and melts at 78—79°.

*Ethyl phenylazo-m-nitrobenzoylacetate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}(\text{N}_2\text{Ph}) \cdot \text{CO}_2\text{Et}$ , crystallises from alcohol in stout, yellowish-brown spangles and melts at 134—135°.

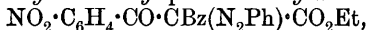
Ethyl acetylcinnamoylacetate (Fischer and Kuzel, Abstr., 1883, 587) and ethyl benzoylmalonate do not condense with diazobenzene chloride.

*Ethyl phenylazodibenzoylacetate*,  $\text{NPh}_2 \cdot \text{CBz}_2 \cdot \text{CO}_2\text{Et}$ , from ethyl dibenzoylacetate and diazobenzene chloride, crystallises from alcohol in slender, yellow prisms and melts at 116°.

*Ethyl phenylacetylbenzoylacetate*,  $\text{CH}_2\text{Ph} \cdot \text{CO} \cdot \text{CHBz} \cdot \text{CO}_2\text{Et}$ , decomposes when distilled in a vacuum; the copper salt crystallises from chloroform or alcohol in bluish needles and melts and decomposes at 194—195°; it condenses with *o*-diazobenzoic acid with elimination of the phenylacetyl group.

*Ethyl benzoyl-p-nitrobenzoylacetate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CHBz} \cdot \text{CO}_2\text{Et}$ , crystallises from alcohol in clusters of slender, white needles and melts at 86—87°.

*Ethyl phenylazobenzoyl-p-nitrobenzoylacetate*,



crystallises from alcohol in yellow needles and melts at 105°.

It is pointed out that where two aromatic acyl groups are attached to ethyl acetate, neither is displaced by the action of diazobenzene chloride; where one fatty and one aromatic group are present, the fatty group is displaced, and where two fatty groups are present, the higher member is displaced; this is probably connected with the strength of the acids, as the displaced groups are all derived from weaker acids than those which remain. Carbethoxy-groups are not displaced.

T. M. L.

**Action of Sulphur Dioxide on *p*-Nitrodiazobenzene Hydroxide.** By ALFRED EKBOM (*Ber.*, 1902, 35, 656—662).—*p*-Nitrobenzenediazo-*p*-nitrobenzenesulphone,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , is formed as a reddish-yellow precipitate on passing sulphur dioxide into an absolute alcoholic solution of *p*-nitrodiazobenzene hydroxide at -5° to 0°; it crystallises from warm ethyl acetate in microscopic needles, decomposes at 135°, is not acted on by light, and is also obtained by the interaction of *p*-nitrodiazobenzenesulphochloride with sodium *p*-nitrobenzenesulphinate. When heated with concentrated hydrochloric acid for 1—2 hours at 100°, it yields a mixture of *p*-chloronitrobenzene, *p*-dinitrodiphenylsulphoxide (m. p. 179—180°), and *p*-nitrobenzenesulphonic acid.

W. A. D.

**Aromatic Diazonium Salts and Ammoniacal Cuprous Oxide Solution.** By DANIEL VORLÄNDER and FELIX MEYER (*Annalen*, 1902, 320, 122—144).—The action of cuprous oxide, dissolved in solutions of ammonia or hydroxylamine, on diazonium salts leads to the formation of azo- and diphenyl derivatives with the elimination of nitrogen. The course of the reaction occurring in the case of substituted aromatic amines depends on the saturated or unsaturated character of their substituents, and not on their negative or positive nature; the presence of unsaturated radicles favours the formation of diphenyl derivatives. The cuprous oxide solution employed is prepared either by dissolving cupric sulphate in excess of hydroxylamine or by treating an ammoniacal solution of this salt with a reducing agent such as hydroxylamine, sulphurous acid, or ferrous sulphate. The diazonium salts from aniline, *o*-, *m*-, and *p*-toluidine, 4-amino-*m*-xylene,  $\psi$ -cumidine, and mesidine, when treated with this reagent, give rise to the corresponding azo-compounds, the yields of 4-azo-*m*-xylene and azo- $\psi$ -cumene being about 90 per cent. of the theoretical. The three chloroanilines and *p*-bromoaniline, when treated in a similar manner, furnish small quantities of their respective azo-derivatives.

Azo-compounds are also the chief products of reaction in the case of *o*-anisidine, *p*-aminophenol, and *p*-phenetidine, an almost quantitative yield being obtained from the first of these bases.

*o*-Nitroaniline, when diazotised and treated with the cuprous oxide solution, yields a small quantity of 2 : 2'-dinitrodiphenyl, together with a trace of *o*-nitrophenol; *p*-nitroaniline, on the other hand, gives an almost theoretical yield of 4 : 4'-dinitrodiphenyl accompanied by a slight amount of nitrobenzene. *p*-Aminobenzoic acid and its ethyl ester furnish their corresponding azo-compounds; ethyl *p*-azobenzoate crystallises in orange-coloured, rectangular plates melting at 144°; Fittica, who formerly obtained an azo-ester from ethyl *p*-nitrobenzoate, described it as crystallising in yellow, prismatic crystals melting at 88°. *m*-Aminobenzoic acid and its ester give rise to azo-compounds; it was not, however, found possible to convert the azo-acid produced into diaminodiphenic acid, and the azo-ester, which distils at 240° under 15 mm. pressure and crystallises in golden-yellow prisms melting at 108—109°, differs from the product described by Golubeff and by Fittica as melting either at 90—92° or at 97°.

When anthranilic acid is diazotised and treated with the cuprous oxide solution, it loses almost all its nitrogen, the principal product of reaction being diphenic acid; its methyl ester, under these conditions, yields methyl diphenate, whilst the ethyl salt gives rise to ethyl benzoate.

The action of ammoniacal cuprous oxide solution on *o*-diazobenzoic acid also leads to the formation of the following bye-products: phenol, salicylic acid, benzoic acid, and probably *o*-chlorobenzoic acid; *o*-azobenzoic acid, however, could not be distinguished. *o*-Diazobenzoic acid, when reduced with a suspension of copper powder in ammonia solution, furnishes a small quantity of diphenic acid; negative results are obtained when the copper or cuprous oxide is suspended in sodium hydroxide solution or when other reducing agents such as ferrous hydroxide are employed. Cuprous hydride, suspended either in

ammoniacal or dilute sulphuric acid solution, reduces *o*-diazobenzoic acid to benzoic acid.  
G. T. M.

**Decomposition of Diazonium Salts by the Aid of Alcohol.** By ARTHUR HANTZSCH (*Ber.*, 1902, 35, 998—1001).—The rationale of the decomposition of diazonium salts has been previously discussed by the author (*Abstr.*, 1900, i, 703), and fresh data and arguments are now adduced in favour of his original explanation and in opposition to Bamberger's more recent conception (this vol., i, 246). If Bamberger's view is accepted and the decomposition is preceded by the formation of a diazonium alkyloxyde,  $\text{ArN}_2\cdot\text{OEt}$ , then in the similar decomposition of diazonium salts by the aid of water it must be assumed that the decomposition is preceded by the formation of a diazonium hydroxide and free mineral acid; in other words, the salt is hydrolysed by the water. But it can be directly proved that the decomposition is not retarded by introducing acid at the beginning of the reaction and does not diminish in velocity as the amount of free acid formed increases, and thus the reaction is in no sense comparable with ordinary cases of hydrolysis.

Similarly, the decomposition of diazonium salts, for example, tri-bromodiazonium sulphate, under the influence of alcohol is not retarded by the presence of an excess of free acid, and cannot therefore be preceded by a decomposition effected by the alcohol. J. J. S.

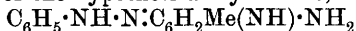
**Action of Cyanoacetic Esters and of their Substitution Derivatives on Diazonium and Tetra-azonium Chlorides.** By G. FAVREL (*Bull. Soc. Chim.*, 1902, [iii], 27, 104—124. Compare *Abstr.*, 1899, i, 58).—The present paper contains a fuller account of the author's work in connection with this subject, some results of which have been already published. The substances obtained by the action of ethyl cyanoacetate on the tetra-azonium chlorides yield the stable  $\beta$ -modification when precipitated from alkaline solution by carbon dioxide, and it is also obtained by dissolving the  $\alpha$ -ester in liquids of high boiling point (aniline, nitrobenzene, &c.). The unstable  $\alpha$ -esters are obtained by precipitating the alkaline solutions of the  $\alpha$ - or  $\beta$ -modification by hydrochloric acid, benzoyl chloride, or acetic anhydride (compare Krückeberg, *Abstr.*, 1894, i, 369).

*Ethyl diphenyldihydrazonocyanoacetate*: the stable  $\beta$ -ester melts at 204—206°, the unstable  $\alpha$ -ester at 234°. *Ethyl diphenyldimethylhydrazonocyanoacetate* is obtained by the action of methyl chloride on the sodium or silver derivative of the preceding compound, and forms yellow lamellæ which melt at 210—212°. *Ethyl diphenyldiethylhydrazonocyanoacetate* forms small, yellow crystals melting at 144—145°. *Ethyl diphenyldihydrazonemonobenzoylcycanoacetate* is obtained by boiling a mixture of xylene and benzoyl chloride in which is suspended the silver derivative of ethyl diphenyldihydrazonocyanoacetate; it melts at 198—200°.

*Methyl diphenyldihydrazonocyanoacetate*.—The  $\alpha$ -ester, obtained in a manner similar to the corresponding ethyl ester, forms a yellow, crystalline powder which melts at 270°. The  $\beta$ -ester melts at 228—230°. When dissolved in boiling nitrobenzene, the  $\beta$ -ester is converted into the

$\alpha$ -ester, which is, in this case, the stable form. *Methyl sodiodiphenyldihydrazonocyanoacetate* forms yellowish, crystalline needles, soluble in methyl alcohol, water, acetone, or pyridine. *Methyl diphenyldimethylhydrazonocyanoacetate* separates from its solution in nitrobenzene or aniline in microscopic needles melting at 276—277°. *Ethyl di-o-tolyldihydrazonocyanoacetate*: The  $\beta$ -ester, obtained by the action of ethyl cyanoacetate on tetrazoditolyl, melts at 224—226°; the  $\alpha$ -ester is obtained by precipitation of the alkaline solutions of the ester with hydrochloric acid. *Ethyl sodiodi-o-tolyldihydrazonocyanoacetate* forms reddish, crystalline needles soluble in acetone or aqueous alcohol. *Ethyl di-o-tolyldimethylhydrazonocyanoacetate* crystallises in faintly yellow plates melting at 220—222°. *Ethyl di-o-tolyldihydrazonemonobenzoylecyanoacetate*, obtained similarly to the diphenyl compound, forms orange crystals melting at 229—230°. *Methyl di-o-tolyldihydrazonocyanoacetate*: the  $\alpha$ -modification, which is the stable one, separates from its solution in nitrobenzene in small, reddish crystals melting at 270—272°. The  $\beta$ -ester melts at 225—227°. *Methyl sodiodi-o-tolyldihydrazonocyanoacetate* forms reddish needles soluble in water, alcohol, acetone, or pyridine. *Methyl di-o-tolyldimethylhydrazonocyanoacetate* crystallises from its solution in nitrobenzene and melts at 266—267°. *Di-o-tolyldihydrazonocyanoacetic acid*, obtained by the hydrolysis of the  $\alpha$ - or  $\beta$ -ester, forms golden-yellow plates which melt at 243—244°. *Methyl di-o-anisylldihydrazonocyanoacetate*: The  $\alpha$ -ester melts at 266—268°; the  $\beta$ -ester melts at 254—255°. *Methyl sodiodi-o-anisylldihydrazonocyanoacetate* forms small, yellow plates, insoluble in water and very slightly soluble in acetone or pyridine; it reacts neither with the alkyl iodides nor with the acyl chlorides. A. F.

**Action of 2:6-Diamidomethylazobenzene on Benzaldehyde.** By FERDINANDO PERUCCHETTI (*Chem. Zeit.*, 1902, 26, 28).—Methyldiamino-2:6-azobenzene condenses with the molecular proportion of benzaldehyde to form a triazine which may be regarded as the condensation product of the hypothetical hydrazone,



$[\text{NH}:\text{Me}:\text{NH}_2=2:3:4]$ , with benzaldehyde. It is a white, difficultly crystallisable substance, which melts with decomposition at 200°. It is insoluble in water, alcohol, ether, or benzene, but is slightly soluble in toluene. It can be diazotised, and yields azo-dyes with resorcinol,  $\beta$ -naphthol, &c. The monoacetyl derivative is yellowish. No substances of a sweet taste are yielded on sulphonation (compare Noelting, *Abstr.*, 1898, i, 155). A. F.

**Action of Hydrogen Chloride on Diphenyl-*p*-azophenylene.** By ERNST BANDROWSKI and A. PROKOPECZKO (*Bull. Acad. Sci. Cracow*, 1901, 441—443).—By the action of dry hydrogen chloride on diphenyl-*p*-azophenylene in benzene solution in the cold, the authors obtained diphenyl-*p*-phenylenediamine hydrochloride and two isomeric *diphenylchlorophenylene-p*-diamines melting at 157° and 106° respectively. They yield two isomeric *diphenyldichloroazophenylenes*, which are crystalline substances of a fine red colour and melt at about 220°. The *azophenylene*, obtained from the diphenyldichlorophenylenediamine

melting at  $157^{\circ}$ , yields with aniline the corresponding *azophenine*,  $C_6Cl_2(NHPh)_2(NPh)_2$  [ $=1:4:2:5:3:6$ ]. The diamine, therefore, contains two free para-positions, whereas the diamine of melting point  $106^{\circ}$  does not.

By the action of hydrogen chloride on the two dichloroazophenylenes, there is obtained, besides the chlorides of the corresponding dichloro-diamines, *diphenyltetrachlorophenylene-p-diamine*,  $C_6Cl_4(NHPh)_2$ , a white crystalline substance which is only slightly soluble in the ordinary organic solvents and has a very weak basic character. A. F.

**Sulphur in Proteids.** By KARL A. H. MÖRNER (*Zeit. physiol. Chem.*, 1902, **34**, 207—338).—In continuation of a research in which it was shown that horny substance when treated with hydrochloric acid gives a good yield of cystin (Abstr., 1900, i, 128), it is now shown that the same is true for a large number of other proteid substances. The yield naturally is not so large, as the total amount of sulphur is smaller than in horn, but the fraction of sulphur contained in the cystin-yielding portion of the molecule, although variable, is usually large. Other parts of the paper are concerned with the other sulphur combinations in the proteid molecule, and with a discussion of the results in reference to the molecular size of proteids. W. D. H.

**Are Proteids, prepared in the usual way, combined with Fat or Fatty Acid.** By E. R. POSNER and WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1902, *Amer. J. Physiol.*, **6**, xxix).—Using Dörmeier's method on quantities of proteid and mucoid from 2 to 13 grams in weight, and following Nerking's procedure, the results were negative. W. D. H.

**Preparation of Carbamide by the Oxidation of Albumin.** By ADOLF JOLLES (*Zeit. physiol. Chem.*, 1901, **34**, 28—31. Compare Abstr., 1901, i, 490).—In reply to Schulz (*ibid.*, i, 780), it is pointed out (1) that the oxidation must take place very slowly in order that trustworthy results may be obtained, (2) that water must be added during the boiling and that the volume of the liquid should never fall below two-thirds of the original, (3) that the precipitation with alcohol must be repeated until the carbamide is obtained free from salts.

J. J. S.

**Phosphoric Acid Esters from Egg-albumin.** By HEINRICH BECHHOLD (*Zeit. physiol. Chem.*, 1901, **34**, 122—127).—When a solution of crystallised egg-albumin is shaken with phosphoryl chloride and sodium hydroxide or normal sodium phosphate, products are obtained which the author regards as true esters of phosphoric acid. A part of these are precipitated on the addition of acetic acid, the remainder on warming. The percentage of phosphorus varies somewhat.

J. J. S.

**Detection of Glucosamine and an Acid derived from an Amino-hexose among the Hydrolytic Products of Serum-albumin.** By LEO LANGSTEIN (*Ber.*, 1902, **35**, 176—178).—The

precipitate obtained by alcohol from a solution of serum-albumin in alkali was treated with 5 per cent. sulphuric acid, and from the resulting solution glucosamine was separated in the form of its pentabenzoyl derivative. The syrup left after precipitation with alcohol, when treated with hydrochloric acid, yielded an *acid* which gave the Molisch reaction, and formed insoluble *barium*, *calcium*, and *lead* salts, and a *benzoyl* derivative, which yielded a *potassium* salt crystallising in yellow nodules.

R. H. P.

**Action of Sodium Ethoxide on Chlorinated Casein.** By THEODOR PANZER (*Zeit. physiol. Chem.*, 1901, **34**, 66—82).—When chlorocasein (Abstr., 1901, i, 780) is treated with an alcoholic solution of sodium ethoxide, part of the chlorine is removed in the form of sodium chloride and a number of simpler products are formed. Among the substances soluble in alcohol is *chlorocaseonic acid*, containing C=50·81, H=5·74, N=11·43, Cl=9·02, and O=23·00 per cent. It dissolves in alcohol, but is precipitated by water, and is also insoluble in ether, benzene, or chloroform. It has not been obtained in a crystalline state and its solutions in alkalis do not coagulate when warmed. It dissolves in cold sodium chloride solutions, but is reprecipitated on warming and again dissolves as the liquid cools. It does not give the more common reactions for proteids, and when hydrolysed with hydrochloric acid yields neither tyrosine nor glutamic acid.

J. J. S.

**Electrolysis of Nucleohiston and Histon Salts.** By W. HUISKAMP (*Zeit. physiol. Chem.*, 1901, **34**, 32—54).—When an aqueous solution of sodium nucleohiston (Abstr., 1901, ii, 461) is subjected to electrolysis, using platinum electrodes, free nucleohiston is almost quantitatively deposited on the anode and practically no secondary reactions occur. The results agree with the view that sodium nucleohiston is ionised in aqueous solutions, but are also, to a certain extent, compatible with the view that the electrolysis is really due to small amounts of mineral salts present as impurities.

Aqueous solutions of histon sulphate prepared by dialysis give the usual sulphion reactions, indicating that the salt is ionised in its aqueous solution. When solutions of histon salts are dialysed for some time, they become faintly alkaline to litmus but not to phenolphthalein, indicating that a certain amount of hydrolysis has taken place. When subjected to electrolysis, histon salts deposit histon on the cathode. Experiments made with casein, globin, and other proteids gave similar results.

When a solution of sodium nucleohiston is added to histon hydrochloride, a precipitate is obtained which probably consists of a compound of nucleohiston and histon; the percentage of ash in the precipitate is only 1·75—1·85.

The fact that sodium nucleohiston is less soluble in solutions containing free sodium ions is in agreement with the ionisation of the salt.

J. J. S.

## Organic Chemistry.

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**New Synthesis of Methane.** By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1902, **134**, 514—516. Compare Abstr., 1901, i, 195).—When a mixture of carbon monoxide (1 vol.) and hydrogen (3 vols.) is passed over reduced nickel at 250°, the two gases are completely converted into methane and water. Carbon dioxide and hydrogen similarly react in the presence of reduced nickel at a somewhat higher temperature, yielding only methane and water.

K. J. P. O.

**Commercial "Benzine."** By A. M. RABINOVITSCH (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 200—201).—The author has submitted to distillation four samples of Russian "benzine" obtained from different sources and having sp. gr. (at 15°/15°) lying between 0·7084 and 0·72095. Of the four fractions distilling: (1) up to 70°, (2) from 70—90°, (3) from 90—100°, and (4) above 100°, the second is in all cases the largest, but the different samples vary considerably in the proportions existing between the fractions. The flash points all lie within the limits -10° and -12°.

T. H. P.

**Commercial Kerosenes from Kieff.** By D. KUDISCH (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 201—202).—The author has examined six samples of commercial kerosene having sp. gr. varying from 0·82300 to 0·82368. The percentages by volume distilling over at different temperatures are: from 137—150°, 5·0 to 6·0; 150—200°, 31·0 to 36·0; 200—270°, 45·5—47·5; above 270°, 13·0 to 15·5. The viscosity at 20° varies from 1·0636 to 1·0727 and at 1° from 1·1909 to 1·205. The flash point limits are 32·5° and 36·0°. All the samples are readily and completely soluble in absolute alcohol and give no solid products when cooled to -20°. The percentages of sulphur in the oils lie between 0·0045 and 0·005°. These data are all in accord with those yielded by good kerosenes.

T. H. P.

**The Wax of Algæ and its relation to Petroleum.** By GUSTAV KRAEMER and ADOLF SPILKER (*Ber.*, 1902, **35**, 1212—1223. Compare Abstr., 1900, i, 73).—Wax is present in all specimens of peat, brown coal, &c., in varying quantities and contains very various amounts of sulphur which owes its origin to the oxidising action of sulphur bacteria. In some cases, the wax is derived from green algæ, and is not then accompanied by siliceous skeletons. When the wax is distilled, it first froths up and evolves carbon dioxide, carbon monoxide, hydrogen sulphide and water containing small amounts of fatty acids in solution. If the distillation be carried out under the ordinary pressure, this stage is followed by the evolution of methane, olefines, and carbon dioxide, whilst a semi-liquid mass of paraffins distils over.

Under diminished pressure, on the other hand, no methane is evolved and a waxy mass, melting at 74—78°, distils over.

By extraction of the wax with alcohol, a fraction soluble in hot alcohol can be obtained which consists of free acid mixed with an ester. The hydrolysis of the wax yields an acid or mixture of acids melting at between 70° and 80° (the melting point varying according to the source of the wax), and corresponding in composition with a fatty acid containing about 22 carbon atoms. The alcoholic component of the ester is a white mass melting at 76—76.5°, and is probably a mixture of homologous alcohols containing 20 to 22 carbon atoms.

Ozokerite appears to represent an intermediate stage between the wax of algæ and petroleum, the products of distillation being of the same kind, although they are formed in different proportions. Ozokerite also contains small amounts of an ester hydrolysable by alcoholic potash.

Pyropissite, which has probably been formed from the remains of successive generations of algæ, contains 25 per cent. of wax and 23.4 per cent. of mineral residue, 72.9 per cent. of which is silica. In this case, a bed of the remains of algæ with siliceous skeletons has probably been covered by a second deposit of green algæ, which vegetated when the depth of water became less, and the whole has then been covered over by a mineral deposit. In the formation of petroleum, this wax would gradually lose methane and carbon dioxide and pass into ozokerite, which in its turn would yield petroleum. The sulphur of petroleum, as already mentioned, is probably to be ascribed to the activity of sulphur bacteria living contemporaneously with the algæ.

A. H.

**Action of Bromine on Methyltrimethylene in Absence of Light.** By NICOLAUS I. DEMJANOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 217—221).—The principal product of the action of bromine on methyltrimethylene in the dark is  $\alpha\gamma$ -dibromobutane, whilst smaller proportions of 1-bromo-1-methyltrimethylene and  $\alpha\gamma\gamma$ -tribromobutane are also formed.

T. H. P.

**Reduction of the Primary Dinitro-hydrocarbons with Aluminium Amalgam.** By GIACOMO PONZIO (*J. pr. Chem.*, 1902, [ii], 65, 197—200).—It is shown that by the reduction of primary dinitro-hydrocarbons with aluminium amalgam, ammonia, and a primary amine, containing the same number of carbon atoms as the dinitro-compound, are obtained, an aldoxime being formed as an intermediate product.

R. H. P.

**Compounds of Alcohol with the Chlorides of Manganese and Cobalt.** By F. BOURION (*Compt. rend.*, 1902, 134, 555—557).—Anhydrous manganous chloride dissolves readily in absolute alcohol, forming a pale rose-coloured solution, which on evaporation deposits large, rose-coloured crystals,  $\text{MnCl}_2 \cdot 3\text{EtOH}$ ; this compound has a sp. gr. 1.35 at 20°/4°, and loses alcohol when exposed to the air, or over sulphuric acid in an exhausted desiccator; when heated at 200° in an atmosphere of carbon dioxide, it loses alcohol, but at a temperature approaching red heat, ethyl chloride is formed.



Cobalt chloride forms a *compound*,  $2\text{CoCl}_2 \cdot 5\text{EtOH}$ , which crystallises in hygroscopic blue needles having a sp. gr.  $1.32$  at  $22^\circ/4^\circ$ . Nickel chloride is but little soluble in alcohol.

K. J. P. O.

**Certain Reactions produced by the Aid of Magnesium Amalgam.** By LÉON MEUNIER (*Compt. rend.*, 1902, 134, 472—473).—Magnesium amalgam attacks cold alcohol, forming magnesium ethoxide and liberating a steady current of hydrogen which is capable of reducing the alkyl iodides to saturated hydrocarbons even more readily than the zinc-copper couple; benzene may with advantage be added to moderate the action. Magnesium ethoxide is a white powder, resembling the corresponding alkali derivatives, and on treatment with dry chlorine yields acetaldehyde, magnesium chloride, and hydrogen chloride.

Magnesium amalgam reacts energetically with acetaldehyde, the reduction being moderated by the addition of benzene or ether; the product, when boiled with alcohol and subsequently filtered, furnishes a solution from which  $\beta\gamma$ -butylene glycol (b. p.  $185^\circ$ ) is isolated by fractional distillation.

G. T. M.

**Pyrogenic Contact-reactions of Organic Compounds. II and III.** By WLADIMIR N. IPATIEFF (*Ber.*, 1902, 35, 1047—1057, 1057—1064. Compare this vol., i, 4).—Iron exerts a catalytic action on the decomposition of alcohol into aldehyde and hydrogen; paraldehyde passed through an iron tube is converted chiefly into methane and carbon monoxide. The action of zinc oxide is very similar to that of metallic zinc.

When *isobutyl* alcohol is passed over heated zinc or brass, 60—70 per cent. is converted into the aldehyde, which can be advantageously prepared in this way. *isoAmyl* alcohol gave a complex mixture of unsaturated hydrocarbons. Allyl alcohol appears to give acetaldehyde as a first product, but this is decomposed into carbon monoxide, propylene, and probably divinyl. Benzyl alcohol gave benzaldehyde, and also benzene and carbon monoxide.

Methyl alcohol is decomposed by heat into trioxymethylene, a decomposition which is facilitated by zinc, but iron causes a further decomposition into hydrogen and carbon monoxide. *isoPropyl* alcohol is decomposed by heat into propylene and acetone, but the latter is further decomposed into methane and carbon monoxide; in presence of brass, the action takes place at a lower temperature and acetone can be separated in considerable quantities.

In presence of graphite, the alcohols are decomposed almost exclusively into an olefine and water, aldehydes being only formed in small quantities. By this method, ethylene and propylene can readily be prepared, whilst *isoamyl* alcohol and *isobutyl* alcohol give mixtures of olefines. Methyl alcohol, under similar conditions, yields considerable quantities of methane.

T. M. L.

**Constitution of Dibutyl and Diconanthyl [Diheptyl] Alcohols.** By MARCEL GUERBET (*Compt. rend.*, 1902, 134, 467—469. Compare Abstr., 1901, i, 182).—The partial oxidation of dibutyl alco-

hol gives rise to dibutyric acid,  $C_8H_{16}O_2$ , a result which shows that the alcohol is a primary one; the ultimate products of oxidation with chromic acid are valeric, butyric, and acetic acids and carbon dioxide; the production of these substances justifies the belief that dibutyl alcohol and dibutyric acid have the following formulæ,

$C_4H_9 \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot OH$ , and  $C_4H_9 \cdot CHMe \cdot CH_2 \cdot CO_2H$ , respectively.

Diönanthyl (diheptyl) alcohol, on gentle oxidation, yields diönanthoic acid,  $C_{14}H_{28}O_2$ , a substance which, on further treatment with chromic acid, gives rise to octoic, heptoic, valeric, butyric, and acetic acids and carbon dioxide; these results indicate that the alcohol and the corresponding acid have the formulæ

$CH_2Me \cdot [CH_2]_2 \cdot CH(C_7H_{15}) \cdot CH_2 \cdot CH_2 \cdot OH$   
and  $CH_2Me \cdot [CH_2]_2 \cdot CH(C_7H_{15}) \cdot CH_2 \cdot CO_2H$ , respectively.

In the production of these alcohols, the coalescence of the two residues takes place at the  $\beta$ -carbon atom with respect to the carbinol group.  
G. T. M.

**Synthesis of Tertiary Alcohols by means of Organo-magnesium Compounds.** By MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 26—31).—The conditions to be observed in order to obtain good yields of tertiary alcohols by the method given by Grignard (Abstr., 1900, i, 382) are as follows: (1) All the materials employed (ketone, alkyl iodide, and magnesium) must be perfectly dry. (2) The three phases of the reaction must all be carried out at as low a temperature as possible, and the whole process may conveniently be completed in one vessel—a large flask. Besides unsaturated hydrocarbons, the secondary products of the reaction comprise secondary alcohols and haloid compounds of high boiling point. The following alcohols have been prepared by the author.

Dimethylisoamylcarbinol (compare Grignard, Abstr., 1901, i, 679) boils at  $155^\circ$  under 745 mm. pressure, has a sp. gr.  $0.8228$  at  $20^\circ/0^\circ$ , and  $n_D$   $1.42085$  at  $20^\circ$ .

Methylethylbutylcarbinol,  $CH_2Pr \cdot CMeEt \cdot OH$ , obtained from methyl butyl ketone, ethyl iodide, and magnesium, is a colourless liquid having the usual odour of tertiary alcohols and dissolving only slightly in water; it boils undecomposed at  $158$ — $160^\circ$  under 745 mm. pressure, and does not solidify when cooled in a mixture of ice and salt; the sp. gr. at  $19^\circ/0^\circ$  is  $0.8273$ , and  $n_D$   $1.42735$  at  $19^\circ$ .

Tripropylcarbinol,  $CPr_3 \cdot OH$ , obtained together with dipropylcarbinol from dipropyl ketone, propyl iodide, and magnesium, boils undecomposed at  $193$ — $195^\circ$  under 737 mm. pressure, and has a sp. gr.  $0.8338$  at  $21^\circ/0^\circ$ , and  $n_D$   $1.43557$  at  $21^\circ$ .  
T. H. P.

**Action of Dilute Acids on Glycols.** By ADOLF LIEBEN (*Monatsh.*, 1902, 23, 60—75).— $\alpha\beta$ -Glycols or the corresponding alkylene dichlorides and dibromides, on treatment with dilute acids or even on heating with water, yield aldehydes and ketones and no alkylene oxide; thus propylene glycol gives propaldehyde and acetone.  $\alpha\delta$ - and  $\alpha\epsilon$ -Dihydric alcohols, for example,  $\alpha\delta$ -dihydroxypentane,  $\alpha\epsilon$ -dihydroxypentane,  $\alpha\epsilon$ -dihydroxyhexane, on treatment with dilute sulphuric acid, yield

cyclic oxides; the corresponding alkylene dichlorides yield the same oxide. These oxides are reconverted into the alkylene dihaloids by the action of concentrated halogen acids.

The  $\alpha$ -glycols break down in a complicated manner. The glycol from isobutaldehyde and formaldehyde,  $\text{CMe}_2(\text{CH}_2\cdot\text{OH})_2$ , gives isovaleraldehyde, methyl isopropyl ketone and a double cyclic oxide,  $\text{C}_{10}\text{H}_{20}\text{O}_2$ , boiling at  $180^\circ$ . The glycol from acetaldehyde and propaldehyde,  $\text{OH}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$ , gives methylethylacetaldehyde (?) and a double oxide,  $\text{C}_{10}\text{H}_{20}\text{O}_2$ , boiling at  $180$ — $185^\circ$ . The glycol from isobutaldehyde,  $\text{CHMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$ , gives a simple oxide,  $\text{C}_8\text{H}_{16}\text{O}$ , which boils at  $120$ — $122^\circ$ , and a double oxide,  $\text{C}_{16}\text{H}_{32}\text{O}_2$ , boiling at  $260$ — $262^\circ$ . The glycol from isobutaldehyde and isovaleraldehyde,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$ , yields a hydrocarbon,  $\text{C}_9\text{H}_{16}$ , a simple oxide,  $\text{C}_9\text{H}_{18}\text{O}$ , and a double oxide,  $\text{C}_{18}\text{H}_{36}\text{O}_2$ , which boils at  $240^\circ$ . The glycol from benzaldehyde and propaldehyde,



gives benzaldehyde and  $\alpha$ -methylhydrocinnamaldehyde. The glycol from benzaldehyde and isobutaldehyde,  $\text{OH}\cdot\text{CHPh}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$ , gives a hydrocarbon,  $\text{CHPh}\cdot\text{CMe}_2$ , which boils at  $182$ — $183^\circ$ , and a formal,  $\text{CH}_2\left\langle\begin{array}{c} \text{O}\cdot\text{CHPh} \\ \text{O}-\text{CH}_2 \end{array}\right\rangle\text{CMe}_2$ , which boils at  $135^\circ$  under 15 mm. pressure.

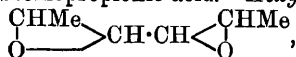
The mechanism of the reactions by which these various substances are formed from the glycols is discussed in the paper. K. J. P. O.

**$\beta$ -Hexanediol and its Derivatives.** By PAUL DUDEN and R. LEMME (*Ber.*, 1902, **35**, 1335—1343).— $\beta$ -Hexanediol, obtained when acetylacetone is reduced with sodium amalgam in the presence of carbon dioxide, is a colourless oil of the consistency of glycerol, boils at  $216$ — $218^\circ$  under 750 mm. pressure, or at  $120$ — $122^\circ$  under 12 mm. pressure, has a sp. gr. 0.9610 at  $20^\circ/4^\circ$  and  $n_D$  1.4475 at  $20^\circ$ ; it forms a diacetate, which is a mobile liquid boiling at  $230^\circ$ , and when boiled with dilute sulphuric acid yields dimethyltetrahydrofurfuran,  $\text{C}_6\text{H}_{12}\text{O}$ , which is a mobile liquid having a characteristic odour and forms a crystalline ferrocyanide and ferricyanide.

The diol, when treated with hydrobromic acid, yields a mixture of the racemic and meso-forms of  $\beta$ -dibromohexane (see Wislicenus, *Abstr.*, 1901, i, 664).  $\beta$ -Hexadiene (*Abstr.*, 1897, i, 262), when treated with bromine (1 mol.), yields  $\beta$ -dibromo- $\beta$ -hexene, which is a strongly refracting oil boiling at  $94$ — $96^\circ$  under 12—14 mm. pressure; when heated with methylamine, this yields 1:2:5-trimethylpyrroline and dimethyldiaminohexene, and when oxidised by permanganate, dibromodihydroxyhexane and then bromopropionic acid.

Dimethyldiaminohexene,  $\text{C}_8\text{H}_{18}\text{N}_2$ , is a yellowish oil which boils at  $175$ — $176^\circ$ , has a sp. gr. 0.8424 at  $20^\circ/4^\circ$  and  $n_D$  1.4556 at  $20^\circ$ , and forms a hygroscopic hydrochloride which crystallises in rosettes of rhombic tablets melting at  $185$ — $187^\circ$ , a platinichloride which crystallises in tablets melting and decomposing at  $215$ — $217^\circ$ , a picrate which crystallises in prisms decomposing at  $218^\circ$ , and a phenylthiocarbamide which crystallises in flat prisms and melts at  $196^\circ$ . Dibromodihydroxyhexane,

$C_6H_{12}O_2Br_2$ , crystallises in tufts of prisms and when oxidised with permanganate yields bromopropionic acid. *Hexylene dioxide*,



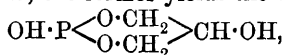
obtained when dibromodihydroxyhexane is boiled with potassium carbonate solution, is a pale yellow, heavy oil which boils at  $176-178^\circ$ .

R. H. P.

**Action of Phosphorus Trichloride on Glycerol and on Glycol.** By P. CARRÉ (*Bull. Soc. Chim.*, 1902, [iii], 27, 264—269).—The author cannot confirm the formation of monoglycerophosphorous acid (compare this vol., i, 9) by the action of phosphorus trichloride on glycerol, and considers that the product of the re-

action consists of the compounds  $\text{P} \begin{array}{c} \text{O} \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{O} \cdot \text{CH}_2 \end{array}$  and  $\text{HO} \cdot \text{P} \begin{array}{c} \text{O} \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{Cl} \end{array}$

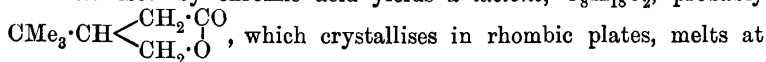
On treatment with water, the former yields the substance



which acts as a monobasic acid; the latter compound also gives rise to a monobasic acid, the study of which is not yet complete.

By the action of phosphorus trichloride on glycol, the compound  $\text{PCl} \begin{array}{c} \text{O} \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} \cdot \text{CH}_2 \end{array}$  is formed, which on treatment with water yields the substance  $\text{OH} \cdot \text{P} \cdot \text{O}_2 \cdot \text{C}_2\text{H}_4$ . The compound  $\text{OH} \cdot \text{PCl} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Cl}$  is probably also formed, but this has not yet been studied. A. F.

**Action of Sulphuric Acid on the [Substituted] Glycerol obtained from Methyltert.butylallylcarbinol.** By ALEXANDER PETSCHNIKOFF (*J. pr. Chem.*, 1902, [ii], 65, 168—187).—An attempt to determine the constitution of the "alcoholoxide," obtained by the action of sulphuric acid on dihydroxymethyltert.butylallylcarbinol,  $\text{CMe}_2 \cdot \text{CMe}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$ . The "alcoholoxide,"  $\text{C}_9\text{H}_{18}\text{O}_2$ , probably  $\text{CH}_2 \begin{array}{c} \text{CH}(\text{OH}) \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CMe}(\text{CMe}_3) \end{array} \text{O}$  or  $\text{CMe}_3 \cdot \text{CMe} \begin{array}{c} \text{O} \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{OH}$ , is a viscous liquid, which has a faint, camphor-like odour, boils at  $214-215^\circ$  under 752 mm. pressure, and has a sp. gr. 0.9716 at  $20^\circ/20^\circ$ . The molecular refraction shows that it is a saturated compound. It forms a *monoacetate*, has no reducing properties, and when oxidised by chromic acid yields a *lactone*,  $\text{C}_8\text{H}_{16}\text{O}_2$ , probably



and can also be obtained by distilling  $\beta$ -methyltert.-butyl-ethylenelactic acid with sulphuric acid. The lactone, when boiled with barium hydroxide, yields the unstable *barium* salt of the corresponding acid,  $(\text{C}_8\text{H}_{15}\text{O}_3)_2\text{Ba}$ .

R. H. P.

**History of the Electrolysis of Organic Acids.** By NIKOLAJ A. BUNGE (*Chem. Zeit.*, 1902, 26, 217—218).—The author refers to

the work done by Kolbe, Kekulé, Wurtz, and others before 1870, and recapitulates the results published by himself in 1870. According to his view, the products formed at the anode are not to be regarded as the result of a simple decomposition of the acid radicle, but are produced by the oxidation of the electrolyte by the oxygen separated at the anode.

J. McC.

**New Compounds of Methylene.** By MARCEL DESCUDÉ (*Compt. rend.*, 1902, 134, 716—718. Compare Abstr., 1901, i, 644, and this vol., i, 149).—The chlorides of all monobasic acids,  $R\cdot COCl$ , react with trioxymethylene in the presence of zinc chloride (compare *loc. cit.*), producing the chloromethyl esters of the acid  $R\cdot CO_2\cdot CH_2Cl$ . From the chlorides of dibasic acids, no such esters were isolated, but the acid chlorides were converted into anhydrides. The chloromethyl esters react with potassium salts of acids above  $160^\circ$ , yielding methylene esters,  $R\cdot CO_2\cdot CH_2Cl + R'\cdot CO_2K = KCl + R\cdot CO_2\cdot CH_2\cdot CO_2\cdot R'$ . By these means there were prepared :

*Chloromethyl valerate*, boiling at  $60^\circ$  under 15 mm. pressure ; *methylene divalerate*, boiling at  $119^\circ$  under 15 mm. pressure ; *chloromethyl o-toluate*, boiling at  $125^\circ$  under 15 mm. pressure ; *methylene di-o-toluate*, melting at  $61\text{--}62^\circ$  ; *chloromethyl m-toluate*, boiling at  $130\text{--}132^\circ$  under 20 mm. pressure ; *methylene di-m-toluate*, melting at  $55\text{--}56^\circ$  and boiling at  $242\text{--}244^\circ$  under 15 mm. pressure ; *chloromethyl p-toluate*, boiling at  $135\text{--}136^\circ$  under 20 mm. pressure ; *methylene di-p-toluate*, melting at  $104^\circ$  ; *chloromethyl phenylacetate*, boiling at  $138\text{--}140^\circ$  under 15 mm. pressure ; *methylene diphenylacetate*, boiling at  $245\text{--}247^\circ$  under 15 mm. pressure ; *methylene acetate-benzoate*,  $CH_3\cdot CO_2\cdot CH_2\cdot CO_2\cdot C_6H_5$ , melting at  $38^\circ$  and boiling at  $255\text{--}260^\circ$  ; *methylene phenylacetate-benzoate*, boiling at  $230^\circ$  under 12 mm. pressure ; *methylene benzoate-o-toluate*, melting at  $51\text{--}52^\circ$  ; *methylene benzoate-m-toluate*, melting at  $36^\circ$ , boiling at  $227^\circ$  under 12 mm. pressure, and *methylene benzoate-p-toluate*, melting at  $74\text{--}75^\circ$  ; the last-mentioned substance was prepared from chloromethyl *p*-toluate and potassium benzoate, and from *chloromethyl benzoate* and (1) *p*-toluic acid or (2) potassium *p*-toluate.

All these substances crystallise in prismatic needles. On adding water to a solution of any of these esters in concentrated sulphuric acid, formaldehyde is evolved.

K. J. P. O.

**Mixed Glycerides in Animal Fat.** By WILLY HANSEN (*Arch. Hygiene*, 1902, 42, 1—15).—When repeatedly crystallised from ether, the stearin of beef and mutton yields a product melting at  $62\cdot5^\circ$  which retains this melting point after recrystallisation from chloroform, benzene, and ether. This substance agrees in properties (saponification number, &c.) with a *distearopalmitin*, and on hydrolysis yields a mixture of acids melting at  $64^\circ$  which also agrees with the mixture obtainable from such a compound. When it is recrystallised from boiling amyl alcohol, it is converted into *tristearin* melting at  $66\cdot8^\circ$ , and yielding pure stearic acid melting at  $69\cdot2^\circ$ . This conversion of *distearopalmitin* into *tristearin* and either tripalmitin or dipalmitostearin by a reaction between several molecules of the fat,

accounts for the so-called double melting point of stearin, which has been observed by many authors. The mixed glycerides obtained from stearin by these authors melt at about 55°, and at a higher temperature yield tristearin, which separates out and then redissolves at a still higher temperature, usually about 71°.

By a similar method, the following compounds have been isolated, the saponification and iodine numbers agreeing in all cases with those required by the constitution assigned: *dipalmitostearin*, melting at 55°; *dipalmito-olein*, melting at 48°; *stearopalmito-olein*, melting at 42°. *Tripalmitin*, melting at 52°, was also obtained, but it is possible that it was formed in a similar manner to tristearin and did not actually occur in the original fat. A. H.

**Composition of Cocoa Butter.** By J. KLIMONT (*Monatsh.*, 1902, 23, 51—59).—This paper contains a more detailed account of work previously published (Abstr., 1901, i, 663). The glyceride,  $C_{51}H_{96}O_6$  (m. p. 25—27°), is stated to be myristopalmito-olein; the saponification number is 211.7, and the iodine number 32.1.

K. J. P. O.

**Unsaturated Acids with two Double Linkings. Homologues of Sorbic Acid.** By OSCAR DOEBNER [and, in part, A. WEISSENORN] (*Ber.*, 1902, 35, 1136—1147. Compare Abstr., 1900, i, 536, and 1901, i, 578).—*β-Vinylacrylic acid*,  $CH_2:CH:CH:CO_2H$ , was prepared by heating acraldehyde, malonic acid, and pyridine for 4 hours at 100°; carbon dioxide was evolved, and a yellowish, syrupy liquid obtained which was poured into dilute sulphuric acid. The acid may be extracted with ether and crystallises in long, colourless, very hygroscopic prisms and short rhombohedra melting at 80° to a mobile liquid, which becomes syrupy at 100—115°, giving methane(?) and liquid hydrocarbons. The alkali salts are very soluble and hygroscopic; the *silver* salt forms small needles; the *calcium* salt is a white, crystalline powder; the *zinc* and *barium* salts are readily soluble; the *lead* salt is a crystalline precipitate.

By the action of bromine, *β-vinylacrylic acid* is converted into *αβγδ-tetrabromovaleric acid*,  $CH_2Br \cdot [CHBr]_3 \cdot CO_2H$ , which crystallises in rhombohedra melting at 160°.

On reduction with sodium amalgam, allylacetic acid,



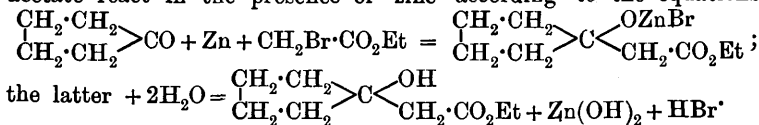
(b. p. 188°), is obtained, and not, as was expected, ethylidenepropionic acid. On oxidation with dilute permanganate, oxalic and racemic acids were formed. On keeping, *β-vinylacrylic acid* polymerises to an acid which decomposes at 300°.

*γ-Methylsorbic acid* could only be obtained in small quantity from *αβ*-dimethylacraldehyde and malonic acid.

*γγ-Dimethylsorbic acid*,  $CH_2Me \cdot CH:CM_e \cdot CH:CH \cdot CO_2H$ , is formed from *α-methyl-β-ethylacraldehyde* and malonic acid, and is a golden-yellow, oily liquid boiling at 165° under 20 mm. pressure; the *silver* salt is a white, and the *copper* salt a pale green, precipitate; the *magnesium* salt is crystalline; a basic *aluminium* salt was obtained.

*γ*-Dimethyl-*γ*-(or *δ*)-hydroxyhydroasorbolactone,  $\text{CH} \begin{smallmatrix} \text{CH} \cdot \text{CO} \\ \text{CMePr}^a \end{smallmatrix} \text{O}$  or  $\text{CHMe} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \text{CHEt} \cdot \text{O} \end{smallmatrix} \text{CO}$ , is formed together with the acid just mentioned, and is a yellow, oily liquid distilling at 145–150° under 20 mm. pressure; the *silver* salt of the corresponding acid,  $\text{C}_8\text{H}_{13}\text{O}_3\text{Ag}$ , is a white powder.  
K. J. P. O.

**Condensation of Ethyl Bromoacetate with *cyclopentanone* and *β*-Methylcyclopentanone.** By NICOLAI A. SPERANSKY (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 17–26).—*cyclopentanone* and ethyl bromoacetate react in the presence of zinc according to the equations:



The hydroxy-ester thus obtained boils at 105–107° under 11 mm. pressure, but could not be prepared in a pure state. When heated with potassium hydrogen sulphate, it gives up water, yielding *ethyl cyclopentanemethylidenecarboxylate*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{C} : \text{CH} \cdot \text{CO}_2\text{Et}$ , which is a colourless, oily liquid having a pleasant odour and boiling at 82–84° under 11 mm. pressure. The free *acid*,  $\text{C}_7\text{H}_{10}\text{O}_2$ , which melts at 49–50° and boils at 122° under 11 mm. pressure, has a fatty-acid odour and dissolves in all the ordinary solvents excepting water. The *silver* salt was prepared and analysed. The *dibromide* of the acid,  $\text{C}_7\text{H}_{10}\text{O}_2\text{Br}_2$ , separates from dilute methyl alcohol in shining crystals melting at 88°. The *amide*,  $\text{C}_6\text{H}_9 \cdot \text{CO} \cdot \text{NH}_2$ , crystallises from aqueous alcohol in transparent plates melting at 144°.

The condensation of ethyl bromoacetate with *β*-methylcyclopentanone is similar to that with *cyclopentanone* and yields *ethyl β-methylcyclopentanolacetate*,  $\begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 - \text{CH}_2 \end{array} > \text{C} \begin{smallmatrix} \text{OH} \\ \text{CH}_2 \cdot \text{CO}_2\text{Et} \end{smallmatrix}$  as a pale yellowish-green liquid, having a pleasant odour and boiling at 113–115° under 11 mm. pressure; the corresponding *methyl* ester boils at 85–90° under 20 mm. pressure. When heated with potassium hydrogen sulphate, the ethyl ester gives up water and forms the ethyl derivative of an unsaturated acid,  $\text{C}_{10}\text{H}_{16}\text{O}_2$ , which is a colourless, oily liquid boiling at 90–92° under 11 mm. pressure. The corresponding *β-methylcyclopentanemethylidenecarboxylic acid*,  $\text{C}_8\text{H}_{12}\text{O}_2$ , boils at 128° under 11 mm. pressure and at 240° with decomposition under the ordinary pressure. The *silver* salt was prepared and analysed. When heated to a high temperature in a sealed tube, the ammonium salt of this acid yields, besides the amide and nitrile of the acid, *γ-methyl-α-methylenecyclopentane*,  $\begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 - \text{CH}_2 \end{array} > \text{C} : \text{CH}_2$ , which has the characteristic odour of the naphth- enes and boils at 96–97° under the ordinary pressure; its sp. gr. is 0.7750 at 16°. When oxidised with potassium permanganate, it gives *β-methylcyclopentanone*.

The *amide* of *β-methylcyclopentanemethylidenecarboxylic acid*,

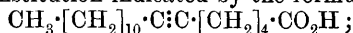
$C_8H_{11}O \cdot NH_2$ , forms plates melting at  $126^\circ$ . The *nitrile*,  $C_7H_{11}CN$ , is a liquid boiling at  $208-210^\circ$  under the ordinary pressure; on reduction, it yields an *amine*,  $C_8H_{15} \cdot NH_2$ , the *oxalate* of which was prepared and analysed. When treated with nitrous acid, the amine gives an *alcohol*,  $C_8H_{15} \cdot OH$ , boiling at  $180^\circ$ . T. H. P.

**Aliphatic and Cyclic Ethyl Citralideneacetoacetates.** HAARMANN and REIMER (D.R.-P. 124227 and 124228).—Aliphatic *ethyl citralideneacetoacetate* (*ethyl  $\psi$ -iononecarboxylate*),  $C_{18}H_{24}O_3$ , prepared by heating on the water-bath a mixture of citral, glacial acetic acid, ethyl acetate, and acetic anhydride, is separated by fractional distillation in a current of steam, the ester being the least volatile product of reaction.

*Ethyl cyclocitralideneacetoacetate* (*ethyl iononecarboxylate*) melts at  $49^\circ$ , boils at  $215^\circ$  under 100 mm. and at  $160^\circ$  under 11 mm. pressure, and has a sp. gr. 1.0387 at  $19^\circ$  and  $n_D$  1.5110; it is produced either by distilling the aliphatic ester in a vacuum or by treating it with concentrated sulphuric acid.

$\beta$ -*Iononecarboxylic acid*,  $C_{14}H_{20}O_3$ , obtained together with  $\beta$ -ionone by the hydrolysis of the aliphatic ester, melts at  $208^\circ$ , and when heated above this temperature evolves carbon dioxide, forming  $\beta$ -ionone; it is sparingly soluble in alcohol, ether, or benzene. G. T. M.

**Constitution of Tariric Acid.** By ALBERT ARNAUD (*Compt. rend.*, 1902, 134, 473—475).—Tariric acid, extracted from the glucoside of the seed of a *tariri* growing in Guatemala, is an isomeride of stearolic acid and has the constitution indicated by the formula



when reduced with hydriodic acid and red phosphorus at  $210^\circ$ , it furnishes stearic acid, whilst its oxidation with potassium permanganate solution or nitric acid leads to the production of adipic and lauric acids. The attack of the oxidising agents is directed towards the unsaturated linking between the fifth and sixth carbon atoms, counting from the carboxyl group (compare Abstr., 1892, 582; 1896, i, 522). G. T. M.

**Halogen Derivatives of Malonic Acid.** By RICHARD WILLSTÄTTER (*Ber.*, 1902, 35, 1374—1378).—Dibromomalonic acid was prepared by exposing to sunlight a solution of malonic acid and bromine in formic acid of sp. gr. 1.2; a vigorous reaction took place and a yield of 90—100 per cent. of the acid was obtained; it crystallises in prisms or needles which melt and decompose at  $130-131^\circ$  and are unchanged in the air. When warmed with water, this acid is quickly converted into dibromoacetic acid (compare Petrieff, Abstr., 1874, 787, and 1878, 490, and Massol, *Ann. Chim. Phys.*, 1894, [vii], 1, 200); the *ammonium* salt forms prisms or plates. *Methyl dibromomalonate*, prepared by brominating methyl malonate, crystallises in lustrous needles or leaflets melting at  $63-65^\circ$ . *Di-iodomalonic acid* is readily obtained by heating malonic acid with iodine and iodic acid in formic acid solution (compare Angeli, Abstr., 1893, i, 307), and is very unstable, decomposing in aqueous solution into iodoacetic acids and giving up iodine to organic solvents; it crystallises from formic acid



in lustrous, pale yellow leaflets melting and decomposing at 119—120°; the *methyl ester* was prepared by the action of potassium iodide on an alcoholic solution of methyl dibromomalonate and crystallised in pale yellow needles melting at 79—80°.

K. J. P. O.

**Synthesis of Dimethylsuccinic Acid in Sunlight.** By WLADIMIR ZERNOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 140—142).—When ethyl  $\alpha$ -iodopropionate, diluted with alcohol, is sealed up in a tube with mercury and shaken in presence of air, an action immediately begins to take place resulting in the formation of diethyl dimethylsuccinate:  $2\text{CHMeI}\cdot\text{CO}_2\text{Et} = \text{CO}_2\text{Et}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et} + \text{I}_2$ . Small quantities of products of higher boiling point are also obtained, these being due to the oxidation of the residue of the ethyl iodo-propionate left after the removal of the iodine.

T. H. P.

**Dioxytariric and Ketotariric Acid.** By ALBERT ARNAUD (*Compt. rend.*, 1902, 134, 547—549. Compare Abstr., 1892, i, 582).—*Dioxytariric acid*,  $\text{CH}_3\cdot[\text{CH}_2]_{10}\cdot\text{CO}\cdot\text{CO}\cdot[\text{CH}_2]_4\cdot\text{CO}_2\text{H}$ , is obtained when tariric acid is oxidised with potassium permanganate or fuming nitric acid; it crystallises in yellow plates melting at 98°; the *dioxime* crystallises in small, colourless needles melting at 166—167°.

When dissolved in concentrated sulphuric acid, tariric acid is converted into *ketotariric acid*,  $\text{CH}_3\cdot[\text{CH}_2]_{10}\cdot\text{CO}\cdot[\text{CH}_2]_5\cdot\text{CO}_2\text{H}$ , which crystallises in pearly leaflets melting at 75°; it forms an insoluble acid *ammonium* salt and an oily *oxime*.

K. J. P. O.

**Synthesis of Muconic Acid from Glyoxal and Malonic Acid.** By OSCAR DOEBNER (*Ber.*, 1902, 35, 1147—1148. Compare Abstr., 1901, i, 188).—Glyoxal (1 mol.) and malonic acid (3 mols.) were heated with pyridine for 3—4 hours on the water-bath. The product was poured into dilute sulphuric acid and the solution extracted with ether. The muconic acid thus obtained crystallised from water in colourless needles melting and decomposing at 292° (compare Baeyer and Rupe, Abstr., 1890, i, 875). For the purpose of identification, it was converted into the silver salt and the dimethyl ester (m. p. 158°).

K. J. P. O.

**Existence of Racemic Compounds in Solution.** By GIUSEPPE BRUNI and M. PADOA (*Atti R. Accad. Lincei*, 1902, 11, i, 212—217).—With the view of obtaining evidence as to the existence of racemic compounds in a dissolved state, the authors have studied the cryoscopic behaviour of the dimethyl esters of diacetyltartaric and diacetyl-racemic acids in solution in benzene, *p*-xylene, ethylene bromide, and bromoform. For low concentrations, both the active and racemic esters give the normal molecular weights in solution, whilst with increasing concentrations more or less association takes place with the different solvents. When a solution of the diacetyltartrate is taken as the solvent, the depressions of freezing point caused by the addition of increasing quantities of the racemic compound indicate values for the molecular weight of the latter considerably greater than those obtained for solutions of similar concentration, but con-

taining only the racemic form. Hence it would seem that in presence of excess of an active compound, the corresponding racemic compound can exist as such in solution.

T. H. P.

**Formaldehyde.** By PAUL N. RAIKOW (*Chem. Zeit.*, 1902, **26**, 135).—When anhydrous potassium carbonate is added to a 40 per cent. aqueous solution of formaldehyde, the solution becomes blue, and on further addition of the solid it becomes yellowish. When the solution is saturated with the carbonate, separation takes place into two clear liquid layers, the upper of which consists of formaldehyde (probably a mixture of different modifications). This liquid has a sp. gr. 1.1902 at 16°, is quite mobile and completely miscible with water, alcohol, or ether, and can be distilled without decomposition. After the main portion has passed over at about 91°, a fraction volatilises at 110° to 112° which condenses to a colourless, gelatinous, voluminous solid. If a perfectly anhydrous liquid be subjected to distillation, this solidification does not take place. The investigation of these modifications of formaldehyde is being continued.

J. McC.

**Physico-chemical Properties of Chloral Hydrate and its Employment in Pharmaceutical Chemistry.** By RICHARD MAUCH (*Arch. Pharm.*, 1902, **240**, 113—134).—At 17.5°, 1 part of water dissolves 4.74 parts of chloral hydrate, and 1 part of absolute alcohol 4.4 of chloral alcoholate. Aqueous solutions were prepared containing 80, 60, and 30 per cent. of chloral hydrate, and a 60 per cent. solution of chloral alcoholate in absolute alcohol; a study was made of the solvent action of these solutions, more particularly of the first two, upon representatives of various classes of organic compounds. Fuller details of these solubilities are given elsewhere (*Inaug. Diss.*, Strassburg, 1898). As a rule, alkaloids dissolve readily in these solutions; so do resins, balsams, and gums; also colouring matters; several proteids, but not silk; several carbohydrates, but not cellulose, whilst starch rather swells up than dissolves. Essential oils dissolve when they do not contain terpenes, not if they do; oils are but little soluble, the drying oils more so than the others; fats and waxes are generally insoluble, and so are hydrocarbons, indiarubber, and guttapercha. Inorganic substances are little soluble; 1 part of iodine dissolves in 560 of the 80 per cent. solution.

Substances that bring about liquefaction when mixed with chloral hydrate dissolve readily in a concentrated aqueous solution of the latter, and *vice versa*. Substances are also soluble which produce liquefaction when warmed with chloral hydrate; they are the more soluble the lower the temperature of liquefaction lies below the melting point of chloral hydrate.

C. F. B.

[**Heptaldehyde and its Homologues.**] SCHIMMEL & Co. (D.R.-P. 126736).—Heptaldehyde boils at 44.4° and 154° under 9 and 747 mm. pressure respectively; it has a sp. gr. 0.8231 at 150°.

*n*-Octaldehyde boils at 60—63° under 10 mm., and at 72° under 20 mm. pressure; it has a sp. gr. 0.827 at 15° and  $n_D$  1.41667; its naphthacinchoninic acid melts at 234°.

*n*-Nonaldehyde boils at 80—82° under 13 mm. pressure and has a sp. gr. 0·8277 at 15° and  $n_D$  1·42452; its naphthacinchonic acid melts at 234°.

*n*-Decaldehyde boils at 97—98° under 15 mm., and at 207—209° under 755 mm., pressure; it has a sp. gr. 0·828 at 15° and  $n_D$  1·4273; its naphthacinchonic acid melts at 237°.

These aldehydes were prepared by distilling mixtures of barium formate with the barium salt of the corresponding acid in a vacuum.

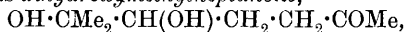
G. T. M.

**Succindialdehyde. II.** By CARL D. HARRIES (*Ber.*, 1902, 35, 1183—1189. See *Abstr.*, 1901, i, 451).—A detailed description of five polymeric modifications of succindialdehyde. A liquid modification is obtained when the dialdehyde is distilled under 10 mm. pressure; from a cryoscopic determination in benzene, it appears to be a termolecular modification. The glassy modification previously described (*loc. cit.*), when heated at about 30° under 0·25 mm. pressure, is quinquemolecular, and termolecular when heated to about 55°; these different modifications of the glassy aldehyde show the same chemical behaviour, but determinations of the molecular refraction indicate that at about 65° the quinquemolecular modification becomes unimolecular. A solid modification, which is crystalline and melts at 64°, is obtained when the molten glassy form at 50° is immersed in water at the same temperature. Another crystalline modification is obtained by the spontaneous evaporation of a benzene solution of the aldehyde; it crystallises in needles and melts at 130—140°. An amorphous form is obtained by the evaporation of an acetone solution containing anhydrous oxalic acid; this is a white powder which partly passes into the simpler modifications at 90—100°.

*Succintetraethylacetal* boils at 137° under 35 mm. pressure, or at 116° under 20 mm. pressure. The dialdehyde, when reduced, yields tetramethylene glycol (butane-1 : 4-diol).

R. H. P.

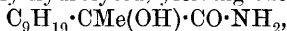
**New Proof of the Constitution of the Synthetical Methylheptenone.** By CARL D. HARRIES (*Ber.*, 1902, 35, 1179—1183).—Methylheptenone,  $\text{CMe}_3\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$ , when oxidised with permanganate, yields *dihydroxymethylheptanone*,



which crystallises in star-shaped clusters of prisms, melts at 66—67°, and boils at 134—136° under 11 mm. pressure. When the oxidation is continued either with chromic acid or permanganate, the *hydroxy-diketone*,  $\text{OH}\cdot\text{CMe}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$ , is obtained; this, which can also be obtained directly by the oxidation of methylheptenone by permanganate in acetone solution, is a colourless oil boiling at 126—127° under 15 mm. pressure and yielding a *disemicarbazone* which melts and decomposes at 226°, and a *dioxime* which crystallises in transparent prisms, sinters at 119°, and melts at 123°. The glycol, when heated with 5 per cent. sulphuric acid, yields *aa*-dimethylacetonylacetone. The formula  $\text{CH}_2\cdot\text{CMe}\cdot[\text{CH}_2]_3\cdot\text{COMe}$  for methylheptenone is therefore to be discarded.

R. H. P.

**Derivatives of Methyl Nonyl Ketone.** By HENRI CARETTE (*Compt. rend.*, 1902, 134, 477—479. Compare Abstr., 1901, i, 367).—Methyl nonyl ketone and hydrogen cyanide slowly combine in the presence of a few drops of concentrated ammonia solution, giving rise to the *cyanohydrin*,  $C_9H_{19} \cdot CMe(OH) \cdot CN$ , a colourless oil which is decomposed even when distilled under reduced pressure. This substance, when heated on the water-bath for 1 hour with concentrated hydrochloric acid, is partially hydrolysed, yielding the *amide*,



a compound crystallising in nacreous lamellæ and melting at 86—87°.

The *acid*,  $C_9H_{19} \cdot CMe(OH) \cdot CO_2H$ , is obtained when the amide or the cyanohydrin is heated for a longer time with excess of concentrated hydrochloric acid; it separates in nacreous crystals melting at 46°. The acid is insoluble in water, but dissolves in the ordinary organic solvents; its ammonium and alkali salts are soluble, and separate from their solutions in nacreous crystals. An *acidic* compound containing nitrogen, also produced during the hydrolysis of the cyanohydrin, forms crystalline lamellæ melting at 185°; its constitution is probably that indicated by the formula  $C_9H_{19} \cdot CMe(NH_2) \cdot CO_2H$ .

G. T. M.

**Derivatives of Arabinose.** By G. CHAVANNE (*Compt. rend.*, 1902, 134, 661—663. Compare Koenigs and Knorr, Abstr., 1901, i, 588, and Fischer and Armstrong, Abstr., 1902, i, 257, 671).—*Bromotriacetyl arabinose*,  $C_5H_6OBr(OAc)_3$ , prepared by mixing arabinose and acetyl bromide together at low temperatures, crystallises in hard, transparent, colourless needles melting at 137°; it is sparingly soluble in light petroleum or methyl and ethyl alcohols, but readily dissolves in ether, acetic acid, chloroform, or benzene in the presence of water; the compound decomposes slowly at the ordinary temperature, more rapidly on heating; it has  $[\alpha]_D - 283^\circ 50'$ , and reduces warm Fehling's solution.

*Chlorotriacetyl arabinose*,  $C_5H_6OCl(OAc)_3$ , produced from acetyl chloride and arabinose at the ordinary temperature, is extracted from the syrupy product by chloroform and precipitated from its solution in this solvent by ether; it is thus obtained as a crystalline powder having  $[\alpha]_D - 224^\circ 49'$ , melting at 148—149°, and reducing warm Fehling's solution. The substance resembles its bromine analogue in solubility and is similarly decomposed by water. These two compounds, when heated with silver acetate in acetic acid solution, yield a compound crystallising in long needles and melting at 80°. *Arabinose phenylhydrazone*, obtained by mixing phenylhydrazine with arabinose dissolved in dilute alcohol, crystallises in white needles melting at 150—151°; it is very sparingly soluble in water.

G. T. M.

**d-Arabinose and d-Arabonic Acid and the Estimation of Arabinose.** By CARL NEUBERG and JULIUS WOHLGEMUTH (*Zeit. physiol. Chem.*, 1902, 35, 31—40).—*l*-Arabinose can be readily prepared from cherry gum. Synthetical processes have to be adopted in order to prepare *d*- and *r*-arabinose in quantity. For the preparation of *d*-arabinose, Wohl's method was found to be the best, namely, from

*d*-glucosoxime, through the stages of *d*-penta-acetylglucononitrile and *d*-arabinosediphenylhydrazine.

*d*-Arabonic acid is most readily made from its diacetamide compound, obtained by treating *d*-penta-acetylglucononitrile, first with ammoniacal silver oxide, then with ammonium sulphide, and finally, at 100°, with fuming hydrobromic acid.

A method of estimating arabinose in urine is described which consists in weighing the hydrazone obtained by adding diphenylhydrazine to the wine, after acidification with acetic acid, evaporation and precipitation of the urates and inorganic salts by addition of hot 96 per cent. alcohol. W. D. H.

**Glucophosphoric Acid.** By P. A. LEVENE (*J. Amer. Chem. Soc.*, 1902, 24, 190—191).—The author has reinvestigated a crystalline substance obtained by Palladin from various seeds (*Zeit. Biol.*, 1894, 31, 199). A copper salt prepared from it contains: C, 16.95; H, 2.85; N, 2.41; P<sub>2</sub>O<sub>5</sub>, 24.10; CuO, 35.66; ash, 57.67 per cent. On hydrolysis with dilute mineral acids, it yields phosphoric acid and a substance which reduces Fehling's solution and gives a crystalline product with phenylhydrazine. E. G.

**Hepta-acetylchloromaltose.** By RICHARD FOERG (*Monatsh.*, 1902, 23, 44—50).—*Hepta-acetylchloromaltose*, C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>Cl(OAc)<sub>7</sub>, was prepared by saturating maltose suspended in acetic anhydride at -21° with hydrogen chloride; it crystallises in large, rhombic leaflets melting at 118—120°, and has  $[\alpha]_D -159^\circ$  at 20° in chloroform solution. The substance is not identical with the isomeride obtained from octoacetylmaltose by Fischer and Armstrong (*Abstr.*, 1901, i, 671) which melts at 64—66°.

*Hepta-acetylmethylmaltoside*, obtained when the preceding compound is shaken with methyl alcohol and silver carbonate, crystallises in leaflets melting at 125—127°. *Hepta-acetylmethylmaltoside* forms elongated leaflets or needles which change at 118° and melt at 121—123°.

K. J. P. O.

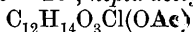
**Melibiose.** By ARMINIUS BAU (*Chem. Zeit.*, 1902, 26, 69—70. Compare *Abstr.*, 1896, i, 453; 1900, i, 77).—The melibiose was prepared from melitriose by boiling with 2—3 per cent. acetic acid solution. When crystallised from water, it contains 2 mols. of water of crystallisation. The rotation of the solution increases on standing, and the final value is  $[\alpha]_D +129.641^\circ$  at 20° (for anhydrous melibiose  $[\alpha]_D$  would be +143.27° at 20°); with increase of concentration, the specific rotation increases slightly.

*Melibiosazone* melts at about 177—179° and decomposes with evolution of gas at about 180°, but these temperatures vary with the previous treatment of the substance. When heated at 95—100°, melibiosazone loses weight slowly, but not a constant amount. Digestion with water at 100° also causes decomposition.

Melibiose can best be recognised by a fermentation process. It is easily and completely fermented by bottom yeast (*Saccharomyces cerevisiæ*), but is not attacked by top yeast. J. McC.

**Hepta-acetylchlorolactose.** By ALBERT BODART (*Monatsh.*, 1902, 23, 1—8).—On treating lactose with acetic anhydride and concentrated

sulphuric acid, an oil was obtained which distilled at 218—225° under 9 mm. pressure; from it petroleum extracts penta-acetyldextrose (m. p. 111.5°). When a suspension of lactose in acetic anhydride is saturated with hydrogen chloride at -20°, *hepta-acetylchlorolactose*,



is obtained; it crystallises from a mixture of benzene and petroleum in colourless needles or prisms sintering at 117.5° and melting at 119—121°, and has  $[\alpha]_D + 71.75^\circ$  at 20° in chloroform solution; acetylphenylhydrazine was the only product of the action of phenylhydrazine. On treating heptaacetylchlorolactose with silver acetate, octoacetylactose,  $\text{C}_{12}\text{H}_{14}\text{O}_3(\text{OAc})_8$ , is obtained, crystallising in plates or needles melting at 86°.

K. J. P. O.

**Decomposition of Carbohydrates by Ferments and Enzymes of Animal and Vegetable Origin.** By WALTHER NIC. CLEMM (*Pflüger's Archiv*, 1902, 89, 517—526).—The effect of various enzymes was tried on starch and glycogen. The resulting sugars were identified by the melting point and solubility of the osazones. Both potato starch and glycogen yield dextrose on treatment with filtered saliva. Dextrose is also formed when the liver of the pig and of the dog containing a large amount of glycogen is kept at 40° for 2 days in presence of thymol. On the other hand, both potato starch and glycogen are converted by malt extract into maltose. Pancreatin, prepared by the addition of alcohol to the pancreatic secretion of a dog, when digested with potato starch yields a sugar the osazone of which agrees in melting point with that of galactose. The secretion employed in this case had undergone slight putrefaction.

The glycerol extract of the pancreas of the pig, on the other hand, converts starch into a sugar, of which the osazone melts at 207—208°, but which does not appear to be identical with dextrose.

A. H.

**Diaminosulphonal.** By ALBERT MANASSE (*Ber.*, 1902, 35, 1372—1374).—On oxidising the phthaliminoethylmercaptate of acetone ( $\text{C}_8\text{H}_4\text{O}_2 \cdot \text{N} \cdot \text{C}_2\text{H}_4 \cdot \text{S}$ ) $_2\text{CMe}_2$  with potassium permanganate in acetic acid solution, *diphthaliminosulphonal*,  $(\text{C}_8\text{H}_4\text{O}_2 \cdot \text{N} \cdot \text{C}_2\text{H}_4 \cdot \text{SO}_2)_2\text{CMe}_2$ , is produced, and crystallises in quadratic leaflets. *Diaminosulphonal hydrochloride*,  $(\text{NH}_2 \cdot \text{C}_2\text{H}_4 \cdot \text{SO}_2)_2\text{CMe}_2 \cdot 2\text{HCl}$ , is formed, when the substance last mentioned is heated with hydrochloric acid under pressure at 150°; it decomposes at 227—233°; the *platinichloride* forms needles decomposing at 248—250°, the *aurichloride*, rhombic leaflets decomposing at 223—224°. *Diaminosulphonal*, obtained from the hydrochloride, crystallises in needles melting at 84—86°, absorbs carbon dioxide from the air, and forms a strongly alkaline aqueous solution; the *diacetyl* derivative crystallises in prisms melting at 165°.

K. J. P. O.

[Compounds of Ethylenediamine and its Derivatives with Mercuric Salts.] CHEMISCHE FABRIK AUF ACTIEN (FORM. E. SCHERING) (D.R.-P. 125095).—*Ethylenediamine mercuricitrate*, produced by mixing together ethylenediamine and mercuric citrate in absolute alcohol, crystallises in white needles sintering at 110° and melting at 137°; it is readily soluble in water, yielding a strongly alkaline solution. The *mercurichloride* obtained by mixing its generators in

aqueous solution forms white needles insoluble in water and alcohol, but dissolving in an aqueous solution of ethylenediamine; it darkens at  $180^{\circ}$  and decomposes at  $225^{\circ}$ . The *mercurisulphate* separates in white needles and is soluble in water, but not in alcohol; it darkens at  $180^{\circ}$  and decomposes at  $210^{\circ}$ . The corresponding *mercuricyanide* and *mercuribenzoate* melt at  $144\text{--}145^{\circ}$  and  $107\text{--}108^{\circ}$ , and crystallise in white needles and lustrous leaflets respectively. The *mercuri-acetate*, *-salicylate*, and *-nitrate* are obtained in a similar manner.

*Diethylethylenediamine mercurinitrate* and the corresponding *mercuri-sulphate*, *-chloride*, *-cyanide*, *-succinate*, and *-salicylate* melt respectively at  $148\text{--}151^{\circ}$ ,  $124\text{--}125^{\circ}$ ,  $159\text{--}160^{\circ}$ ,  $108\text{--}110^{\circ}$ ,  $128\text{--}130^{\circ}$ , and  $181\text{--}183^{\circ}$ .

*Piperazine mercuri-acetate*, obtained by treating mercuric acetate with piperazine in alcoholic solution, is moderately soluble in water; it darkens at  $188^{\circ}$  and melts at  $198^{\circ}$ .

These double salts may also be prepared by treating the mercuric salts with the carbonates of the organic amines. They have antiseptic properties and do not coagulate albumin. G. T. M.

**The Oxime of Diacetoneamine;  $\beta\gamma$ -Diamino- $\beta$ -methylpentane.** By MORIZ KOHN (*Monatsh.*, 1902, 23, 9—21. Compare *Abstr.*, 1901, i, 194, 367).—Diacetoneamino-oxime has a feeble reducing action on Fehling's solution, gives with copper sulphate a deep blue coloration, and a silver mirror with silver nitrate; with excess of mercuric chloride, a precipitate is formed which is soluble in hot water; the *sulphate*,  $2\text{C}_6\text{H}_{14}\text{ON}_2\cdot\text{H}_2\text{SO}_4$ , crystallises in needles decomposing at  $210\text{--}220^{\circ}$ ; the *oxalate*,  $2\text{C}_6\text{H}_{14}\text{ON}_2\cdot\text{H}_2\text{C}_2\text{O}_4$ , in needles decomposing at  $214^{\circ}$ .

*$\beta\gamma$ -Diamino- $\beta$ -methylpentane* ( $\beta\gamma$ -diaminoisobutane),



is prepared by reduction of a solution of the amino-oxime in dilute acetic acid by sodium amalgam; it forms a mobile, ammoniacal liquid boiling at  $147\text{--}155^{\circ}$  and absorbs carbon dioxide from the air, forming a carbamate; the *hydrochloride* and *platinichloride* were prepared. The *compound* of the former, with mercuric chloride,  $\text{C}_6\text{H}_{16}\text{N}_2\cdot 2\text{HCl}\cdot 3\text{HgCl}_2$ , crystallises in needles melting at  $181\text{--}183^{\circ}$ .

The *dicarbamide*,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , prepared from the hydrochloride and silver cyanate, is a pale yellow solid; the *nitrate* crystallises in needles decomposing at  $138\text{--}140^{\circ}$ .

K. J. P. O.

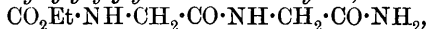
**Derivatives of Diaminoacetic Acid and Diaminomalononic Acid.** By RICHARD WILLSTÄTTER (*Ber.*, 1902, 35, 1378—1387).—*Methyl tetramethyldiaminoacetate*,  $\text{CH}(\text{NMe}_2)_2\cdot\text{CO}_2\text{Me}$ , obtained by the interaction of methyl di-iodoacetate and excess of dimethylamine in solution in dry benzene, is a mobile, colourless oil, with an odour of formaldehyde, boiling at  $57\text{--}58^{\circ}$  under 12.5 mm. pressure; it is readily soluble in most solvents, immediately reduces silver nitrate and acidified permanganate solutions, gives no insoluble picrate, platini-chloride, or aurichloride, is not attacked by cold aqueous alkali carbonates, but is decomposed by boiling aqueous alkali carbonates or by alkali hydroxides; with concentrated platinic chloride, dimethylamine

is immediately eliminated. Methyl dibromoacetate and dimethylamine react in a different manner, yielding *dibromoacetyldimethylamide*,  $\text{CHBr}_2 \cdot \text{CO} \cdot \text{NMe}_2$ , which crystallises in prisms, melts at  $79-80^\circ$ , and boils at  $128^\circ$  under 12 mm. pressure; with excess of dimethylamine, *hydroxydimethylaminoacetyldimethylamide*,  $\text{OH} \cdot \text{CH}(\text{NMe}_2) \cdot \text{CO} \cdot \text{NMe}_2$ , is formed as a colourless oil boiling at  $80^\circ$  under 12 mm. pressure, and is soluble in all solvents; it is volatile with steam, reduces silver nitrate, and is immediately decomposed by alkalis and acids; with concentrated platinic chloride, half the dimethylamine is immediately eliminated.

*Methyl tetramethyldiaminomalonate*,  $\text{C}(\text{NMe}_2)_2(\text{CO}_2\text{Me})_2$ , is prepared by the action of dimethylamine on methyl dibromomalonate in benzene solution at a low temperature; it crystallises from ether in rhombic plates, melts at  $83-85^\circ$ , is volatile with steam, and boils without decomposing; it is immediately decomposed by alkalis and acids and by methyl iodide. When hydrolysed by prolonged boiling with water, the dimethylamine salt of mesoxalic acid is obtained together with *tetramethyldiaminomalic acid*,  $\text{C}(\text{NMe}_2)_2(\text{CO}_2\text{H})_2$ , which was separated from the salt by recrystallisation from absolute alcohol; it forms a crystalline powder melting and decomposing at  $133^\circ$ , and immediately reduces silver nitrate; concentrated platinic chloride effects the elimination of the whole of the dimethylamine.

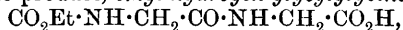
K. J. P. O.

**Derivatives of Glycine, Alanine, and Leucine.** By EMIL FISCHER (*Ber.*, 1902, 35, 1095—1106. Compare Abstr., 1901, i, 675).—The substance formerly described as carbaminoglycylglycine ethyl ester is really *ethyl glycylglycinamidocarboxylate*,



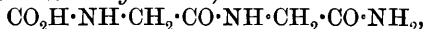
as it is not identical with the *carbaminoglycylglycine ethyl ester*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , crystallising in slender needles and melting at  $163^\circ$  ( $165^\circ$  corr.), which is obtained by the action of potassium cyanate on glycylglycine ethyl ester hydrochloride.

When diethyl glycylglycinocarboxylate is hydrolysed with 1 mol. of aqueous sodium hydroxide at the ordinary temperature, it is probable that carboxyethyl group first attacked is the same as that affected by ammonia; the product, *ethyl hydrogen glycylglycinocarboxylate*,



crystallises from water or alcohol in small, flexible needles, melts at  $140^\circ$  (corr.), decomposes at  $200^\circ$ , and yields crystalline *copper* and *silver* salts. If 2 mols. of alkali are used in the hydrolysis and the liquid is boiled and subsequently acidified with hydrochloric acid, *glycylglycinocarboxylic acid*,  $\text{CO}_2\text{H} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , is obtained; it crystallises from water in stellate aggregates of needles, melts and decomposes at  $208^\circ$  (corr.), and yields a granular *silver* salt.

*Glycylglycinamidocarboxylic acid*,



obtained by hydrolysing its ester (ethyl glycylglycinamidocarboxylate) with 1 mol. of aqueous sodium hydroxide at the ordinary temperature, crystallises from warm water in small, colourless leaflets or prisms and melts and decomposes at  $195^\circ$  (corr.).



The action of guanidine on diethyl glycyglycinecarboxylate gives the *guanidine* salt,  $C_6H_{11}O_4N_3$ , of an *acid*,  $C_5H_6O_4N_2$ , which can be considered as the anhydride of glycyglycinecarboxylic acid; the salt crystallises from methyl alcohol in short, colourless prisms and melts at  $224^\circ$ .

*Diethyl glycyglycyl-leucinecarboxylate*,

$CO_2Et \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CH(C_4H_9) \cdot CO_2Et$ ,  
obtained by heating diethyl glycyglycinecarboxylate with leucine ethyl ester for 36 hours at  $130-135^\circ$ , crystallises from water in colourless prisms and melts at  $109.5^\circ$  (corr.).

Glycyglycine ethyl ester, when acetylated, yields the *acetyl* derivative,  $NHAc \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et$ , which crystallises from alcohol and melts at  $152^\circ$ ; when its hydrochloride is shaken in aqueous solution with carbonyl chloride dissolved in toluene, it gives *carbonyldiglycylglycine ethyl ester*,  $CO(NH \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et)_2$ , which crystallises from water and melts and decomposes at  $233^\circ$  (corr.). *Carbonyldiglycyglycine*,  $CO(NH \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H)_2$ , obtained by hydrolysing the ester, crystallises from water and melts and decomposes at  $232^\circ$  (corr.); *carbonyldiglycyglycinamide*,

$CO(NH \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot NH_2)_2$ ,

crystallises from water in sheaves of needles melting and decomposing at  $270^\circ$ .

The product of the action of either ethyl or methyl alcohol and hydrogen chloride on alanine anhydride is a syrup which cannot be made to crystallise; that obtained by using ethyl alcohol readily interacts, however, with ethyl chlorocarbonate to form *diethyl alanylalaninecarboxylate*,  $CO_2Et \cdot NH \cdot CHMe \cdot CO \cdot NH \cdot CHMe \cdot CO_2Et$ , which crystallises from ether, on adding light petroleum, in colourless needles melting at  $70^\circ$  (corr.).

*Leucylleucine*,  $NH_2 \cdot CH(C_4H_9) \cdot CO \cdot NH \cdot CH(C_4H_9) \cdot CO_2H$ , obtained by heating at  $100^\circ$  leucine anhydride (leucinimide) with hydrobromic acid saturated at  $0^\circ$ , crystallises from water in small, colourless needles (with  $1\frac{1}{2}H_2O$ ), sinters at  $260^\circ$ , and melts slightly above  $270^\circ$ .

Of the foregoing substances, only three, namely, ethyl glycyglycinamidecarboxylate, diethyl glycyglycyl-leucinecarboxylate and carbonyldiglycyglycinamide, give the biuret reaction. W. A. D.

**Synthesis of  $\zeta$ -Aminoheptonic Acid.** By ALBERT MANASSE (*Ber.*, 1902, 35, 1367—1372).—The starting point of the synthesis of  $\zeta$ -aminoheptonic acid was  $\epsilon$ -phenoxyamylamine (see Gabriel, *Abstr.*, 1892, 717); the latter was converted into  $\epsilon$ -*phenoxyamylphthalimide*,  $OPh \cdot [CH_2]_5 \cdot N : C_8H_4O_2$ , by heating with phthalic anhydride at  $200^\circ$ ; the phthalimide crystallises in elongated leaflets melting at  $72-73^\circ$ . By the action of concentrated hydrobromic acid, the phenoxy-compound is converted into  $\epsilon$ -*bromoamylphthalimide*, which forms white, flattened needles melting at  $61^\circ$ . *Ethyl phthaliminoamylmalonate*,

$C_8H_4O_2 \cdot N \cdot [CH_2]_5 \cdot CH(CO_2Et)_2$ ,

prepared by heating the last-mentioned substance in alcoholic solution with sodium ethoxide and ethyl malonate, was ill-defined and was converted into  $\zeta$ -amino-*n*-heptonic acid,  $NH_2 \cdot [CH_2]_6 \cdot CO_2H$ , by boiling with concentrated hydrobromic acid; from the hygroscopic hydro-

bromide thus obtained, the acid was prepared by treatment with silver oxide; it melted at 186—187° (compare Wallach, Abstr., 1900, i, 590). By heating the acid at 190° in a vacuum, a glassy, insoluble substance,  $C_7H_{15}ON$  (?), was formed.

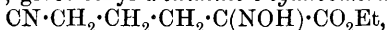
$\epsilon$ -Piperidinoamylamine,  $C_5NH_{10}[CH_2]_5 \cdot NH_2$ , is prepared by heating  $\epsilon$ -bromoamylphthalimide with piperidine and then boiling the product with hydrobromic acid. It is an oil boiling at 238—239° under 759 mm. pressure; the *platinichloride* crystallises in golden-yellow needles decomposing at 228°.

$\epsilon$ -Anilinoamylphthalimide,  $NHPh \cdot [CH_2]_5 \cdot N : C_8H_4O_2$ , is prepared from aniline and  $\epsilon$ -bromoamylphthalimide; it crystallises in pale yellow needles, melts at 113—114°, and dissolves in most organic solvents; by boiling with hydrochloric acid, it yields the *hydrochloride* of  $\epsilon$ -anilinoamylamine, which forms needles melting at 218°. By the action of alcoholic potassium hydrosulphide on  $\epsilon$ -bromoamylphthalimide, a mixture of sulphide and mercaptan is formed; the latter,  $\epsilon$ -phthaliminoamyl mercaptan,  $C_8H_4O_2 \cdot NO \cdot [CH_2]_5 \cdot SH$ , crystallises in white needles melting at 49.5° and is decomposed into phthalic acid and aminoamyl mercaptan by boiling hydrochloric acid.  $\epsilon$ -Phthaliminoamyl disulphide,  $(C_8H_4O_2 \cdot N \cdot [CH_2]_5)_2S_2$ , prepared by the action of iodine on the mercaptan just described, melts at 60°;  $\epsilon$ -phthaliminoamyl sulphide,  $(C_8H_4O_2 \cdot N \cdot [CH_2]_5)_2S$ , is prepared by the action of  $\epsilon$ -bromoamylphthalimide on the sodium derivative of the mercaptan; it crystallises in slender needles melting at 98°. K. J. P. O.

Anhydrides of  $\alpha$ -Amino-fatty Acids. By E. HOYER (*Zeit. physiol. Chem.*, 1902, 34, 347—352. Compare Cohn, Abstr., 1900, i, 466).—2:5-Dimethylpiperazine (Bamberger and Einhorn, Abstr., 1897, i, 259) is obtained when lactimide, prepared by Fischer's method, is reduced with sodium and alcohol. This confirms Cohn's results.

J. J. S.

Synthesis of  $\alpha\epsilon$ -Diaminohezoic Acid. By EMIL FISCHER and FRITZ WEIGERT (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 270—275).—Ethyl  $\gamma$ -cyanopropylmalonate, when treated with ethyl nitrite in the cold, gives ethyl  $\alpha$ -oximino- $\delta$ -cyanovalerate,



at first as an oil, which soon solidifies, and then melts at 74°. When reduced with sodium in alcoholic solution, this compound gives  $\alpha\epsilon$ -diaminohezoic acid,  $NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$ , which was isolated by successive transformations into the phosphotungstate and picrate. The *picrate* can be crystallised from hot water in thick needles which darken at 230°. The *hydrochloride*, prepared from the picrate by means of hydrochloric acid, was obtained in the crystalline form, softens at 182°, and melts between 183° and 186° (corr.). The *phenylcarbinide* has also been prepared from the hydrochloride; it is formed in colourless needles melting at 182—185° (corr.).

These derivatives of  $\alpha\epsilon$ -diaminohezoic acid have been compared with the corresponding compounds of natural lysine; the only observable differences are in the optical activity (the synthetical substances being inactive) and, slightly, in the melting points. The authors therefore regard this acid as *r*-lysine.

J. McC.

**Constitution of the so-called Nitrosourethane.** By JULIUS W. BRÜHL (*Ber.*, 1902, 35, 1148—1152).—The refractive index of solutions of nitrosourethane in methyl or ethyl alcohol and in ethyl acetate was determined. From these values, the molecular refraction was obtained of nitroso-urethane; in methyl alcohol,  $[n]_a$  27·18 and  $[n]_D$  27·49; in ethyl alcohol,  $[n]_a$  26·32 and  $[n]_D$  26·51; in ethyl acetate,  $[n]_a$  26·22 and  $[n]_D$  26·04; or as mean value,  $[n]_a$  26·57 and  $[n]_D$  26·68.

Owing to the colour of the solutions, the molecular dispersion could not be determined. The molecular refraction of the group  $N_2O$  is obtained by subtracting molecular refraction (calculated) of the complex,  $C_3H_6O''O$ , from the experimental value for nitrosourethane; it amounts to 8·87 for  $[n]_a$  and 8·90 for  $[n]_D$ ; the values 9·28 and 9·35 were respectively obtained from measurements of the refractive index of nitrosoethylurethane (*Abstr.*, 1898, ii, 362). Nitrosourethane and nitrosoethylurethane must consequently possess a similar constitution. Since the value for  $N_2O$  in the case of these substances differs widely from that found in the case of nitrosodialkylamines, it is concluded

that nitrosourethane is diazourethane,  $\begin{smallmatrix} N \\ | \\ O \end{smallmatrix} \gg NH \cdot CO_2Et$ , and nitrosoethyl-

urethane, diazoethylurethane,  $\begin{smallmatrix} N \\ | \\ O \end{smallmatrix} \gg NEt \cdot CO_2Et$  (compare Hantzsch, *Abstr.*, 1899, i, 685, and this vol., i, 222). K. J. P. O.

**Action of Alkyl Haloids on the Thiocarbonates of Secondary Amines [Tetra-alkylformocarbthialdines].** By MARCEL DELÉPINE (*Compt. rend.*, 1902, 134, 714—716. Compare *Abstr.*, 1901, i, 518, and this vol., i, 199).—Dialkylthiourethanes,  $NR_2 \cdot CS \cdot SR$ , are obtained when an alkyl haloid (1 mol.) is added to an alcoholic solution of a secondary amine (1 mol.) and carbon disulphide (1 mol.); the reaction proceeds with development of heat and is complete after an hour; the mixture is poured into water, when the thiourethane separates as crystals or as an oil. The reaction is  $NR_2 \cdot CS \cdot S \cdot NH_2R_2 + R'X = NR_2 \cdot CS \cdot SR' + NH_2R_2X$ . The dialkylthiourethanes are pale yellow, crystalline solids of low melting point, which are destitute of basic properties, and thus differ from the isomeric iminothiocarbonic esters (*loc. cit.*), than which they have a higher boiling point and a higher sp. gr.; their odour resembles that of phenols:

Constitution.	Sp. gr. 0°/4°.	Melting point.	Boiling point.
$NMe_2 \cdot CS_2Me$ .....	—	47°	243°
$NMe_2 \cdot CS_2Et$ .....	1·1255	47	252
$NEt_2 \cdot CS_2Me$ .....	1·0977	2	256
$NPr_2 \cdot CS_2Me$ .....	1·0475	0	275

The *piperidyl* derivative,  $C_5NH_{10} \cdot CS_2Me$ , melts at 33—34°; the *hydroisoquinoline* derivative,  $C_9NH_{10} \cdot CS_2Me$ , at 70°; the *dibenzyl* derivative,  $N(CH_2Ph)_2 \cdot CS_2Me$ , at 55°, and the *p-nitrobenzyl* derivative,



at 60°. These thiourethanes are only attacked by ammonia and amines at 300°. On oxidation with nitric acid, a secondary amine, carbon dioxide, sulphuric acid, and an alkylsulphonic acid are produced. On

reduction of the compound  $\text{NMe}_2 \cdot \text{CS}_2 \text{Me}$  with sodium and absolute alcohol, sulphur, sodium mercaptide, trimethylamine, and dimethyl-methylenediamine,  $\text{CH}_2(\text{NMe}_2)_2$ , are obtained. K. J. P. O.

**Alkali Cyanamides.** DEUTSCHE GOLD- & SILBER-SCHNEIDE-ANSTALT (D.R.-P. 124977).—Sodium cyanamide,  $\text{CN}_2\text{Na}$ , is produced either by adding sodamide gradually to fused sodium cyanide or by passing dry ammonia into a mixture of molten cyanide and metallic sodium. Potassium cyanamide,  $\text{CN}_2\text{K}$ , is prepared from potassamide and potassium cyanide, whilst mixtures of sodamide and potassium cyanide or potassamide and sodium cyanide yield the sodium potassium cyanamide,  $\text{CN}_2\text{NaK}$ . G. T. M.

**New Method for Characterising Pseudo-acids applied to the Alkyl Oximinocynoacetates.** By PAUL TH. MULLER (*Compt. rend.*, 1902, 134, 475—476).—The alkyl oximinocynoacetates containing the isonitroso-radicle and the negative group cyanogen, have distinctly acid properties. Their electric conductivity is comparable with that of acetic acid; they can be titrated with alkali hydroxides in the presence of phenolphthalein, and their alkali salts do not undergo hydrolytic dissociation. Determinations of the molecular refraction of these substances and their sodium salts with respect to the  $\alpha$ - and  $\gamma$ -hydrogen lines and the D-sodium line show that the values of these constants for the free acids are about 3.26 units lower than the corresponding numbers obtained with the salts. The results are tabulated. G. T. M.

**The Pseudo-acids.** By PAUL TH. MULLER (*Compt. rend.*, 1902, 134, 664—665).—The equation representing the neutralisation of any acid by sodium hydroxide being  $\text{RH} + \text{NaOH} = \text{RNa} + \text{H}_2\text{O}$ , then, on applying to this system the law of mixtures, the following relationship between the molecular refractions of reagents and product is obtained, namely, refraction  $\text{RNa}$  - refraction  $\text{RH}$  = refraction  $\text{NaOH}$  - refraction  $\text{H}_2\text{O}$  = a constant  $K$ . The values of this constant vary between 1.50 and 1.60, and the law is found to hold in the case of a large number of acids resembling acetic acid. If, however, the structure of the radicle  $\text{R}$  varies during neutralisation, the generalisation is no longer applicable, and the values of  $K$ , experimentally determined, differ considerably from 1.55. Abnormal values of the constant were obtained with isonitrosoacetone, isonitrosocamphor, and the esters of oximinocynoacetic and isonitrosomalonic acids (compare preceding abstract); similar variations were observed in the molecular dispersion. These substances fall into the category of pseudo-acids, their constitution undergoing transformation during their conversion into neutral salts. G. T. M.

**Aminoacetonitrile.** By AUGUST KLAGES (*J. pr. Chem.*, 1902, [ii], 65, 188—197).—Aminoacetonitrile,  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CN}$ , obtained by treating the cyanohydrin of formic acid with cold alcoholic ammonia, is a colourless oil which boils at (about)  $58^\circ$  under 15 mm. pressure and forms a hydrochloride crystallising from alcohol and melting at  $165^\circ$ . With

phenylcarbimide, it yields *phenylhydantoinitrile*,  $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CN}$ , which crystallises in lustrous leaflets and melts at  $165^\circ$ . *Hippuronitrile* crystallises from alcohol and water in lustrous leaflets and melts at  $144^\circ$ . *Cinnamoylaminoacetoneitrile*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CN}$ , crystallises in laminae or needles, melts at  $154^\circ$ , and when boiled with alcoholic hydrogen chloride yields the corresponding *ester*; this melts at  $108^\circ$  and is easily hydrolysed to the *acid*, which crystallises in needles or laminae melting at  $193^\circ$ . Formaldehyde and aminoacetoneitrile condense to form methyleneaminoacetoneitrile (m. p.  $129^\circ$ ), which, from cryoscopic determinations in naphthalene and chloroform, is a bimolecular compound; the unimolecular *compound* melts at  $82\text{--}83^\circ$ , and the corresponding *benzylidene* derivative at  $72^\circ$ .

*Diethylaminoacetoneitrile*,  $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CN}$ , obtained when aminoacetoneitrile is boiled with diethylamine for 6 hours, is a colourless liquid with a camphor-like odour; it boils at  $70\text{--}71^\circ$  under 24 mm. pressure and forms a *hydrochloride* which crystallises in colourless, lustrous needles melting at  $192^\circ$ . The *methiodide* crystallises from alcohol in colourless needles and melts at  $205^\circ$ . The *aurichloride* of the nitrile of methyl-diethylbetaine,  $\text{C}_7\text{H}_{14}\text{N}_2\cdot\text{HAuCl}_4$ , crystallises from water and melts at  $99\text{--}100^\circ$ . The *ethiodide* crystallises from alcohol, melts at  $179^\circ$ , and when treated with moist silver oxide yields a *base* which forms a crystalline *picrate*, *aurichloride*, and *mercurichloride*.

*α-Diethylaminopropiononitrile*,  $\text{NEt}_2\cdot\text{CHMe}\cdot\text{CN}$ , obtained from lactonitrile and diethylamine, is an oil which boils at  $81^\circ$  under 27 mm. pressure and has a sp. gr. 0.857 at  $16^\circ/4^\circ$ . The *aurichloride* crystallises in needles melting at  $126^\circ$ , and the *picrate* melts at  $102^\circ$ . The *methiodide* melts and decomposes at  $212^\circ$ , and the methochloride forms an *aurichloride* which melts at  $109\text{--}110^\circ$ . R. H. P.

**Preparation of Hydrogen Cyanide in the Electric Furnace and Transformation of Atmospheric Nitrogen into Ammonia.** By HANS HOYERMANN (*Chem. Zeit.*, 1902, 26, 70—71).—In view of the observations made by Berthelot and by Moissan that hydrogen cyanide can be obtained from acetylene and nitrogen, the author led mixtures of these gases through hollow carbon electrodes into the arc light, and found that hydrogen cyanide is formed in large quantity. It is also produced from acetylene and ammonia, or from benzene and nitrogen. The best result is obtained when the mixture contains 2 volumes of nitrogen per volume of acetylene.

When a mixture of calcium fluoride and aluminium is heated to redness in a carbon crucible, a residue is obtained which, when treated with hot water, gives off a large quantity of ammonia. Aluminium fluoride is volatilised, and the residual mass apparently consists of calcium nitride ( $\text{Ca}_3\text{N}_2$ ), the nitrogen being obtained from the air. The same mixture, heated in a porcelain tube in a current of nitrogen, did not give the same result. J. McC.

**Basic Properties of Oxygen. III.** By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1902, 35, 1201—1212. Compare this vol., i, 112).—I. *Quadrivalency of oxygen*.—It seems probable that the compound of ether with magnesium methiodide,  $\text{MgMe}\cdot\text{OEt}_2\text{I}$ , described

by Grignard, is a true oxonium compound of simple type, the existence of such a compound, whilst no compound of the type  $R_3OI$  is known, being rendered possible by the fact that the group  $MgMe$  has a greater affinity for oxygen and is more easily separated from iodine than the methyl group itself.

II. *Salts of Ferrocyanic Acid with the simplest Organic Oxygen Compounds.*—When an alcoholic solution of ferrocyanic acid is evaporated slowly, an oil is left which solidifies in large, transparent tablets containing 3 mols. of alcohol, and decomposes in the air. The oil itself probably contains 4 mols. of alcohol. This renders it probable that the crystalline compound obtained by Buff (*Annalen*, 1854, **91**, 253) by passing hydrogen chloride into an alcoholic solution of ferrocyanic acid is in reality a *double salt* of the alcohol compound of ferrocyanic acid with alcohol hydrochloride,  $Fe(CN)_6H_4(EtOH)_4 + 2Et \cdot OH, HCl$ , and the properties of the compound agree fully with this constitution. Ferrocyanic acid also forms a *compound* with methyl alcohol which crystallises in lustrous, efflorescent needles.

Similarly, the compound described by Than (*Annalen*, 1858, **107**, 315) as ethyl platinocyanide with water of crystallisation, is in reality the salt of cyanoplatinous acid with ethyl alcohol,  $Pt(CN)_4H_2 \cdot 2EtOH$ , and since this acid forms very stable oxonium salts it will probably be of great value as a reagent.

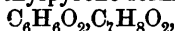
Ferrocyanic acid not only combines with alcohol and with ether, as previously shown, but also forms mixed compounds. When a solution of the acid in methyl alcohol is precipitated by ether, the *compound*,  $H_4Fe(CN)_6 \cdot C_4H_{10}O \cdot CH_4O$ , separates out in rhombic plates. It is probable that the substance obtained by Buff by dissolving his compound in alcohol and precipitating with ether was also a substance of this class.

When acetone is added to a solution of ferrocyanic acid in methyl alcohol, a *compound* of ferrocyanic acid with acetone,  $H_4Fe(CN)_6 \cdot C_3H_6O$ , is formed, which crystallises in plates. The complex acids may conveniently be prepared from the acidified solutions of their salts by treatment with cineol, followed by purification of the resulting oxonium salt, and removal of the cineol by distillation or extraction with ether.

III. *Compounds of Phenols with Organic Oxygen Compounds.*—Many compounds of phenols with bases are already known. Pyridine unites with 1 mol. of quinol to form the *compound*  $C_5H_5N \cdot C_6H_6O_2$ , which crystallises in needles and melts at  $81-83^\circ$ . Quinoline unites with quinol to form the *compound*  $2C_9H_7N \cdot C_6H_6O_2$ , which crystallises in flat prisms melting at  $98-99^\circ$ . With pyrogallol, it forms the *compound*  $3C_6H_3N \cdot C_6H_6O_3$ , crystallising in flat prisms and melting at  $56-57^\circ$ .

Similar compounds are also formed by phenols with oxygen compounds. Cineol and resorcinol form the *compound*  $C_6H_6O_2 \cdot 2C_{10}H_{18}O$ , which crystallises in long, lustrous, rhombic plates melting at  $80-85^\circ$ . Cineol and pyrogallol form the *compound*  $C_6H_6O_3 \cdot C_{10}H_{18}O$ , which crystallises in prisms and has no definite melting point. The *compound* of quinol with ethyl oxalate,  $C_6H_6O_2 \cdot C_6H_{10}O_4$ , forms large plates and has no definite melting point. The *compound* of quinol and cinnamaldehyde,  $C_6H_6O_2 \cdot 2C_9H_8O$ , forms faintly yellow needles melting at

53—55°. Quinol and dimethylpyrone form the compound



which crystallises in prisms and melts at 107—109°. The compound of quinol with *tert.* amyl alcohol,  $\text{C}_6\text{H}_6\text{O}_2, \text{C}_5\text{H}_{12}\text{O}$ , is unstable and loses the alcohol when heated. The compound of quinol with trimethylcarbinol,  $\text{C}_6\text{H}_6\text{O}_2, \text{C}_4\text{H}_{10}\text{O}$ , resembles that with *tert.* amyl alcohol.

IV. Compound of Oxalic Acid with Oxygen Compounds.—Cinnamaldehyde oxalate,  $\text{C}_2\text{H}_2\text{O}_4, 2\text{C}_9\text{H}_8\text{O}$ , forms tetrahedral crystals melting at 60—62°. Cineol oxalate,  $\text{C}_2\text{H}_2\text{O}_4, 2\text{C}_{10}\text{H}_{18}\text{O}$ , decomposes at 50°.

A. H.

Preparation of a Soluble Prussian Blue. By J. MATUSCHEK (*Chem. Zeit.*, 1902, 26, 92—93).—On heating a solution of potassium ferricyanide with oxalic acid, a blue colour is developed, and on evaporation a blue deposit is obtained. The blue substance, which has the formula  $\text{Fe}_7(\text{CN})_{18}$ , is formed according to the equation:  $14\text{K}_3\text{Fe}(\text{CN})_6 + 42\text{C}_2\text{H}_2\text{O}_4 + 3\text{H}_2\text{O} = 2\text{Fe}_7(\text{CN})_{18} + 42\text{C}_2\text{O}_4\text{HK} + 48\text{HCN} + 3\text{O}$ . Some decomposition also takes place in another way, for the solution contains, besides this blue compound, a ferric salt which imparts a yellow colour to it. The blue compound is easily soluble in water, but is insoluble in alcohol. It retains the potassium hydrogen oxalate simultaneously deposited with great tenacity, so that this can only be removed by repeated washing with dilute alcohol.

A similar decomposition can be brought about by sunlight instead of heat, and it has been proved that the oxygen of the air takes no part in the reaction.

J. McC.

New Reactions of Organometallic Compounds. V. By EDMOND E. BLAISE (*Compt. rend.*, 1902, 134, 551—553. Compare this vol., i, 164).—Magnesium alkyl bromides react with ethylene oxide, forming together with a small amount of a primary alcohol of the type  $\text{R}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$  (compare Grignard and Tissier, this vol., i, 198), mainly the bromohydrin of glycol; the addition of the magnesium alkyl bromide to the ethylene oxide takes place in two ways: (i)  $\text{R}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{MgBr}$  and (ii)  $\text{R}\cdot\text{Mg}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Br}$ .

The esters of  $\alpha$ -brominated fatty acids condense with trioxy-methylene in the presence of zinc, producing the esters of  $\beta$ -hydroxy-acids; thus from ethyl  $\alpha$ -bromoisobutyrate is obtained *ethyl hydroxypivalate*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ , which boils at 85—87° under 16 mm. pressure, and yields an acid crystallising in long needles. With phosphorus pentabromide, *ethyl bromopivalate* is obtained as an oil of agreeable odour boiling at 89—90° under 25 mm. pressure.

K. J. P. O.

Chemistry of Mercury. III. By HEINRICH LEY and KONRAD SCHAEFER (*Ber.*, 1902, 35, 1309—1316. Compare Abstr., 1899, ii, 485; 1900, i, 382).—The mercuric derivatives of the organic oxy-acids undergo hydrolytic dissociation in aqueous solutions, and their electrical conductivities are of the same order as those of the acids themselves.

The stability of the mercury-nitrogen linking is far greater than that of the metal with oxygen, and the aqueous solutions of the mer-

curic derivatives of amides, imides, and similarly constituted substances do not give the reactions of the  $\text{Hg}''$  ion. The equilibrium of the system  $2\text{R}\cdot\text{CO}\cdot\text{NH}_2 + \text{HgCl}_2 \rightleftharpoons 2\text{HCl} + (\text{R}\cdot\text{CO}\cdot\text{NH})_2\text{Hg}$  was studied in the case of the homologous amides of the acetic acid series by the electrolytic method; for since the ionisation of mercuric chloride is very slight, the agent chiefly concerned in the transmission of the current is the hydrochloric acid, and hence the electrical conductivity is a measure of the amount of mercury derivative produced. The electrical conductivities  $\mu_{64}$  of solutions containing  $N/32$   $\text{HgCl}_2$  and  $N/16$  amide were 7.8, 5.2, 5.1, and 5.3 for formamide and its successive homologues up to butyramide. The mercury derivative,  $\text{Hg}(\text{NH}\cdot\text{CO}\cdot\text{C}_3\text{H}_7)_2$ , of the latter amide separates from water as a white, crystalline mass. A more dilute solution was necessary in the case of chloroacetamide, and the system  $N/64$   $\text{HgCl}_2$  +  $N/32$   $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}_2$  gave  $8.8\mu_{128}$ . The substitution of cyanogen for chlorine increases the tendency to the formation of a mercury derivative, the system  $N/32$   $\text{HgCl}_2$  +  $N/16$   $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$  giving  $53.5\mu_{64}$ . This abnormal result accords with the behaviour of the amide towards freshly precipitated mercuric oxide, the amount of the latter substance dissolved being in excess of that required by the formula  $\text{Hg}(\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CN})_2$ , and corresponding more nearly with  $\text{CN}\cdot\text{CH}(\text{Hg}\cdot\text{OH})\cdot\text{CO}\cdot\text{NH}_2$ . The values of  $\mu_{64}$  obtained with urea, urethane, and biuret are 5.3, 5.2, and 5.8 respectively. The system  $N/32$   $\text{HgCl}_2$  +  $N/16$  succinimide gives  $40.2\mu_{64}$ , whilst the value of the constant with camphorimide is 45.3. These results indicate that the stability of the mercury compounds of imides exceeds that of the corresponding derivatives of the amides.

The electrical conductivity of the system  $N/32$   $\text{HgCN}_2$  +  $N/16$   $\text{HCl}$  is 355, whilst that of the acid is 369; the amount of hydrogen cyanide set free, although appreciable, is very small. When, however, nitric acid is employed, there is no appreciable metathesis, the electrical conductivity,  $355.1\mu_{32}$ , being identical with that of the acid itself. These results place mercuric cyanide entirely outside the category of imides and points to the existence in this compound of a stable linking between mercury and carbon.

G. T. M.

**Silver Derivatives of Acid Amides and Imides.** By HEINRICH LEY and KONRAD SCHAEFER (*Ber.*, 1902, 35, 1316—1319. Compare Titherley, *Trans.*, 1901, 79, 391).—The yellow precipitate which is produced on adding silver nitrate to an aqueous or dilute alcoholic solution of urethane in the presence of sodium hydroxide, rapidly becomes orange coloured, and finally, when dried, forms a brick-red powder. The red salt probably contains silver attached to nitrogen; it dissolves in excess of sodium hydroxide solution, yielding a solution from which the original substance is reprecipitated on dilution.

Phenylurethane and the corresponding benzyl analogue, when treated with silver nitrate and a small quantity of sodium hydroxide, yield deep red precipitates which rapidly become black. G. T. M.

**Compounds of Antimony Pentachloride with Organic Acids.** By ARTHUR ROSENHEIM and WILLY LOEWENSTAMM (*Ber.*, 1902, 35, 1115—1130. Compare this vol., i, 68).—With antimony pentachloride,



organic acids and hydroxy-acids form crystalline additive compounds which contain 1 mol. of the pentachloride for each carboxyl group. On heating, these compounds decompose, yielding acid chlorides. The additive compounds derived from hydroxy-acids (and dibasic acids) give substances in which the hydroxylic hydrogen has been replaced by the group  $\cdot\text{SbCl}_4$ . Esters yield similar additive compounds. The number of mols. of antimony pentachloride in the additive compound appears to depend on the number of carbonyl groups present; thus, ethyl acetoacetate combines with  $2\text{SbCl}_5$ , whereas ethyl metacarbonate combines only with  $\text{SbCl}_5$ . The view is expressed that in the additive compounds the oxygen of the carbonyl group has become quadrivalent.

The additive compounds are prepared by mixing chloroform solutions of mol. proportions of the acid (or ester) and antimony pentachloride, and are very hygroscopic, crystalline substances, readily soluble in chloroform, carbon tetrachloride, &c. The compounds with *acetic acid*,  $\text{CH}_3\cdot\text{CO}_2\text{H}, \text{SbCl}_5$ , and with *ethyl acetate*,  $\text{CH}_3\cdot\text{CO}_2\text{Et}, \text{SbCl}_5$ , crystallise in white needles; those with *propionic* and *valeric* acids cannot be isolated, and when kept in chloroform solution are converted into *additive* compounds of antimony pentachloride and the acid chlorides,  $\text{CH}_2\text{Me}\cdot\text{COCl}, \text{SbCl}_5$  and  $\text{CH}_3\cdot[\text{CH}_2]_3\cdot\text{COCl}, \text{SbCl}_5$ , which crystallise in hygroscopic, transparent plates.

The *compound* with benzoic acid,  $\text{C}_6\text{H}_5\cdot\text{CO}_2\text{H}, \text{SbCl}_5$ , forms stable, white needles, melting at  $71^\circ$ , and on heating yields benzoyl chloride. Phenylacetic acid gives an unstable *product* crystallising in yellow needles.

The additive compound with oxalic acid (*loc. cit.*) yields a substance to which is now ascribed the formula  $(\text{CO}_2\cdot\text{SbCl}_4)_2$ , and not that previously stated (compare Anschütz and Evans, *Abstr.*, 1888, i, 424). By addition of a chloroform solution of antimony pentachloride to methyl oxalate suspended in boiling chloroform, a *compound*,  $\text{C}_2\text{O}_4(\text{CH}_2\cdot\text{SbCl}_4)_2$ , is obtained which crystallises in white, hygroscopic plates. Ethyl oxalate yields a crystalline *additive* compound,  $\text{C}_2\text{O}_4\text{Et}_2, 2\text{SbCl}_5$ , which easily loses hydrogen chloride with the production of a *substance*,  $\text{C}_2\text{O}_4(\text{CH}_2\cdot\text{CH}_2\cdot\text{SbCl}_4)_2$ , crystallising in white plates.

From malonic acid, a *compound*,  $\text{CH}_2(\text{CO}_2\text{H})_2, \text{SbCl}_5$ , crystallising in pale brown needles was prepared with some difficulty; ethyl malonate yielded with ease a *compound*,  $\text{CH}_2(\text{CO}_2\text{Et})_2, 2\text{SbCl}_5$ , which formed very hygroscopic, white needles. From succinic acid was obtained a stable *additive* product with  $2\text{SbCl}_5$ , crystallising in needles, and from ethyl succinate a *compound*,  $\text{C}_2\text{H}_4(\text{CO}_2\text{Et})_2, 2\text{SbCl}_5$ , also crystallising in needles. Phthalic acid yields the *compound*  $\text{C}_6\text{H}_4(\text{CO}_2\cdot\text{SbCl}_4)_2$ , which forms white, prismatic crystals.

Ethyl carbonate gives a *compound* with  $\text{SbCl}_5$  crystallising in hygroscopic needles. The following hydroxy-acids react with antimony pentachloride with evolution of hydrogen chloride: lactic acid yields a *compound*,  $\text{SbCl}_4\cdot\text{O}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , forming prisms which decompose at  $132^\circ$ ; ethyl lactate, the corresponding *ethyl* ester crystallising in prismatic plates; mandelic acid, a *compound*,  $\text{SbCl}_4\cdot\text{O}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ , crystallising in needles. From salicylic acid, an *additive compound*,

$\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}\cdot\text{SbCl}_5$ , is obtained, crystallising in pale yellow needles which very easily decompose into hydrogen chloride, and the acid,  $\text{SbCl}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , which crystallises in very soluble, reddish-yellow needles, melts at  $154^\circ$ , decomposes at about  $185^\circ$ , does not give a reaction with ferric chloride, and forms a series of salts; the *lead* and *thallium* salts form dark yellow, insoluble crystals, the *silver* salt an amorphous yellow powder; the salts of the alkaline earths are soluble and crystalline; the *potassium* salt forms small, lustrous, red prisms, the *ammonium* salt reddish-purple prisms, the *cæsium* salt insoluble, yellow needles. When mol. proportions of antimony pentachloride and salicylic acid are heated together for many hours in chloroform solution, a compound,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{O} \\ \text{CO}_2 \end{smallmatrix}\rangle\text{SbCl}_5$ , is obtained; it crystallises in slender, orange-yellow, insoluble needles melting and decomposing at  $194^\circ$ , and is only decomposed after prolonged boiling with alkalis. Methyl salicylate and antimony pentachloride form an *additive* compound,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}\cdot\text{SbCl}_5$ , crystallising in dark yellow needles; this is readily converted into the *ester*,  $\text{SbCl}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ , which forms prisms resembling potassium dichromate and melting at  $135^\circ$ ; the *ethyl* ester melts at  $121^\circ$ .

Tartaric acid yields an *acid*,  $\text{C}_2\text{H}_2(\text{O}\cdot\text{SbCl}_4)_2(\text{CO}_2\text{H})_2$ , crystallising in white, very hygroscopic needles; the *ethyl* ester forms aggregates of hygroscopic prisms.

Ethyl citrate yields an *additive* compound,  
 $\text{CO}_2\text{Et}\cdot\text{C}(\text{OH})(\text{CH}_2\cdot\text{CO}_2\text{Et})_2\cdot 3\text{SbCl}_5$ ,  
 crystallising in large, white needles.

Ethyl acetoacetate gives an *additive* compound with  $2\text{SbCl}_5$ , crystallising in white, hygroscopic needles.

Tungsten hexachloride does not form additive compounds, but reacts with hydroxy-acids with evolution of hydrogen chloride, thus with methyl salicylate a *compound*,  $\text{WCl}_4(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me})_2$ , is formed; it crystallises in large, deep red crystals. Tungsten pentachloride, on the other hand, readily forms additive compounds with development of heat.

K. J. P. O.

**Dicyclohexyl and Dimethyldicyclohexyl.** By NICOLAI KURSANOFF (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 221—226).—*Dicyclohexyl*,  $\text{C}_6\text{H}_{11}\cdot\text{C}_6\text{H}_{11}$ , prepared by the action of sodium on iodocyclohexane, is an oily, faintly-smelling liquid, which boils at  $235^\circ$  under 752 mm. pressure and solidifies to a crystalline mass in a mixture of ice and salt; it has the sp. gr. is  $0.8777$  at  $0^\circ/0^\circ$  and  $0.8644$  at  $20^\circ/0^\circ$ . It is not acted on by alkaline permanganate or by a mixture of sulphuric and nitric acids.

*Dimethyldicyclohexyl*,  $\text{C}_6\text{H}_{10}\text{Me}\cdot\text{C}_6\text{H}_{10}\text{Me}$ , obtained by the action of sodium on iodomethyldicyclohexane, boils undecomposed at  $264^\circ$  under 761 mm. pressure and at  $148\text{—}149^\circ$  under 30 mm. pressure, and solidifies to a glassy mass when cooled in liquid air; it has the sp. gr.  $0.8924$  at  $0^\circ/0^\circ$  and  $0.8789$  at  $20^\circ/0^\circ$ , and  $[\alpha]_D -3.44'$ . In its behaviour towards reagents, it resembles dicyclohexyl.

The methods of preparation of these compounds give rise also to considerable quantities of the corresponding naphthenes and naph-

thylenes; the latter are formed by the splitting off of hydrogen iodide from the iodonaphthene, whilst the reducing action of sodium in presence of hydriodic acid yields the naphthenes. T. H. P.

$\Delta^{13}$ . Dihydrotoluene and a Modification of Wagner's Oxidation Rule. By CARL D. HARRIES [and, in part, ERNST ATKINSON] (*Ber.*, 1902, 35, 1166—1176).—Methylcyclohexenonehydroxylaminoxime (Abstr., 1901, i, 194), when oxidised by mercuric oxide, yields a mononitroso-compound,  $C_7H_{12}O_2N_2$ , which is a white, crystalline substance melting to a blue oil at  $106-108^\circ$ ; the dibenzoyl derivative of the oxime is a colourless oil, and the oxalate a white, crystalline mass. Hexahydro-*m*-tolylenediamine (*loc. cit.*) forms a crystalline nitrate and a dibenzoyl derivative which melts between  $247^\circ$  and  $270^\circ$ . Hexahydro-*m*-tolylenediaminediphenylcarbamide,  $C_{21}H_{26}O_2N_4$ , crystallises in rhombic rods and melts between  $210^\circ$  and  $240^\circ$ .  $\Delta^{13}$ . Dihydrotoluene (*loc. cit.*), when oxidised with permanganate in aqueous solution, yields oxalic and succinic acids, and, when in aqueous acetone solution, dihydroxymethylcyclohexanone (see this vol., i, 378).

A dihydro-*m*-xylene has been prepared from the hydroxylaminoxime of dimethylcyclohexenone by methods analogous to those previously described (*loc. cit.*). Hexahydro-*m*-xylylenediamine is a colourless liquid which boils at  $103-105^\circ$  under 27 mm. pressure, absorbs carbon dioxide, and forms a hydrochloride which crystallises in colourless, rhombic, pyramidal prisms with a high melting point.

Hexahydro-*m*-xylylenediaminediphenylcarbamide crystallises in needles and melts at  $247^\circ$ . The phosphate of the diamine is a syrup, and when distilled, yields the dihydro-*xylene*, which is a light yellow oil boiling at  $126-128^\circ$  under a pressure of 750 mm.

From a discussion of the results, it is shown that the products of the oxidation of an unsaturated compound do not necessarily contain as many "oxidised" carbon atoms as those which were doubly linked in the original compound. It also follows from this that terpinene is  $\Delta^{14}$ -menthanediene, and is identical with the synthetical terpene prepared by Baeyer from ethyl succinylsuccinate. R. H. P.

The Configuration of the Benzene Nucleus. By WILHELM VAUBEL (*Chem. Zeit.*, 1902, 26, 244—245).—Objection is taken to the conclusions arrived at by Graebe (this vol., i, 209) as to the figure representing the benzene molecule. Facts are stated in support of the Vaubel-Marsh configuration, three tetrahedra above and three below a plane, which explains (a) the different behaviour of *o*- and *p*-derivatives from that of the *m*-compounds; (b) the influence of *m*-substitution; and (c) that molecular rearrangement may take place and thus evidence of enantiomorphism is in most cases lost. The author regards his figure as satisfactorily accounting for the oscillating single and double bond of Kekulé's hypothesis. J. McC.

Action of Copper Nitrate on Benzene. By NICOLAI P. WASSILIEFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 33—37. Compare *J. Russ. Phys. Chem. Soc.*, 1894, 26).—The reaction between copper nitrate and benzene proceeds slowly at  $100^\circ$ , but the best results are obtained by heating in sealed tubes at  $170-190^\circ$  for 12—18 hours.

The products obtained are nitrobenzene, picric acid, several nitro- and other compounds not yet investigated, and an *acid* of the  $C_nH_{2n-2}O_{2n}$  series. This acid melts in a sealed capillary tube at 98—100° and dissolves readily in water or alcohol and slightly in ether; when heated with alcohol and hydrochloric acid, it yields ethyl oxalate. T. H. P.

**Reaction between Benzene and Cellulose.** By A. M. NASTUKOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 231—235).—When a concentrated sulphuric acid solution of Swedish filter paper is shaken in a separating funnel with benzene, the latter reacts with the cellulose, and on decomposing the solution with water a dark brown powder is obtained which is insoluble in the ordinary solvents, but is partially soluble in cold nitric acid, the portion not dissolved undergoing nitration. From the analysis of different fractions of the nitrated compound, the author supposes that the first product of the reaction between the benzene and cellulose is tetraphenylcellulose,  $C_6H_5O_5Ph_4$ , and that this undergoes sulphonation and, on treatment with nitric acid, nitration. The two following nitrated products were separated and analysed: (1)  $C_{360}H_{292}O_{103}N_{20}S$ , resulting from the introduction into 12 tetraphenylcellulose molecules of 20 nitro-groups and one  $SO_3H$  group in place of 21 hydrogen atoms; when dried at 105—110°, this compound loses  $12H_2O$  and assumes the formula  $C_{360}H_{268}O_{91}N_{20}S$ ; (2)  $C_{360}H_{288}O_{114}N_{24}S_2$ , obtained from 12 molecules of tetraphenylcellulose by the replacement of 24 hydrogen atoms by  $NO_2$  groups and of two hydrogen atoms by  $SO_3H$  groups. T. H. P.

**Derivatives of 3:4:5-Tribromonitrobenzene.** By C. LORING JACKSON and A. H. FISKE (*Ber.*, 1902, 35, 1130—1133).—By the action of sodium methoxide in the cold, 3:4:5-tribromonitrobenzene is converted into 1-methoxy-2:6-dibromo-4-nitrobenzene (m. p. 122°), which, on reduction, yields a *base*,  $OMe \cdot C_6H_2Br_2 \cdot NH_2$ , melting at 64—65° (compare Staedel, *Abstr.*, 1883, 663); the *hydrochloride* was analysed. When boiled with sodium methoxide in methyl alcoholic solution, the tribromonitrobenzene is transformed into a 3:5-dibromo-4-methoxyazoxybenzene,  $ON_2(C_6H_2Br_2 \cdot OMe)_2$ , which crystallises in pale yellow needles melting at 214°.

Sodium ethoxide in the cold converts the tribromonitrobenzene into 1-ethoxy-2:6-dibromo-4-nitrobenzene (m. p. 58—59°), which, on reduction, yields the corresponding amino-derivative (m. p. 107°); Staedel (*loc. cit.*) gives 108° and 67° as the melting points respectively of these two substances. When boiled with sodium ethoxide in ethyl alcoholic solution, a 3:5-dibromo-4-ethoxyazoxybenzene is obtained, crystallising in pale yellow needles melting at 163°.

On treatment with a boiling mixture of fuming nitric and sulphuric acids, 3:4:5-tribromo-1:2-dinitrobenzene,  $C_6HBr_3(NO_2)_2$ , is formed from tribromonitrobenzene; it crystallises in large, monoclinic prisms melting at 160°. K. J. P. O.

**Monoiodo- and Monobromo-derivatives of the Aromatic Hydrocarbons.** KALLE and Co. (D.R.-P. 123746).—Sulphur iodide,  $S_2I_2$ , and the corresponding bromide react with aromatic hydrocarbons

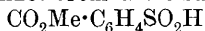
in the presence of nitric acid, giving rise to iodo- and bromo-derivatives respectively. The mono-substituted compounds are exclusively produced except in the case of durene which furnishes a dibromo-derivative.

Benzene, *o*-xylene, mesitylene, and naphthalene, when dissolved in light petroleum and warmed with nitric acid of sp. gr. 1.34 and powdered sulphur iodide, yield the corresponding moniodo-derivatives, naphthalene giving rise to  $\alpha$ -iodonaphthalene together with smaller quantities of the  $\beta$ -iodo-compound and  $\alpha$ -nitronaphthalene.

G. T. M.

**Toluene-*o*-sulphonic Chloride and the *o*-Sulphonic Chlorides of Etheral Benzoates.** BASLER CHEMISCHE FABRIK (D.R.-P. 124407).—Toluene-*o*-sulphonic chloride is obtained from toluene-*o*-sulphonic acid by treating this with chlorine in the presence of dilute sodium hydroxide or hydrochloric acid solution, the temperature being kept below 35°.

The *o*-sulphonic chloride,  $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ , of methyl benzoate, produced in a similar manner from the *o*-sulphonic acid,



(m. p. 98—99°), melts at 64—65°.

G. T. M.

**Preparation of Triphenylmethane.** By JAMES F. NORRIS and GRACE MACLEOD (*Amer. Chem. J.*, 1901, 26, 499—505).—Norris and Saunders (Abstr., 1901, i, 198) have shown that if the product of reaction of benzene on carbon tetrachloride in presence of aluminium chloride be purified by crystallisation, triphenylchloromethane is obtained, whilst by distillation triphenylmethane is produced. By the action of benzene on chloroform in presence of aluminium chloride, triphenylmethane is also obtained when the crude product is distilled. If the aluminium additive compound be carefully decomposed with water in presence of a large volume of carbon disulphide, then on evaporation of the carbon disulphide solution, crystals of triphenylcarbinol are obtained along with an uncrystallisable oil. When triphenylmethane is treated with aluminium chloride in carbon disulphide solution and a current of oxygen is aspirated through the mixture, crystals of triphenylcarbinol are produced as well as a thick oil. By the action of aluminium chloride on triphenylcarbinol, triphenylchloromethane is obtained. The composition of the oil produced by the reaction between benzene and chloroform is very complex and the various constituents have not yet been identified; it probably contains diphenylchloromethane.

Triphenylmethane is probably produced during the distillation as a result of the reduction of the triphenylcarbinol by the uncrystallisable oil.

J. McC.

**Condensation Products from 1 : 8-Dinitronaphthalene soluble in Alkali Hydroxides.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 125133).—1 : 8-Dinitronaphthalene, when heated with sodium hydroxide solutions of salicylic acid, *p*-aminosalicylic acid, and *p*-aminophenol, gives rise to condensation products which are soluble in this medium and precipitated on the addition of hydrochloric acid.

G. T. M.

**2:4-Dinitrostilbene and its Derivatives.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 124681).—Although the methyl group of the nitrotoluenes and similar mononitro-derivatives does not react with aromatic aldehydes, yet condensation occurs when the nucleus contains two nitro-groups.

2:4-Dinitrostilbene,  $C_6H_5 \cdot CH:CH \cdot C_6H_3(NO_2)_2$ , is produced by heating benzaldehyde and 2:4-dinitrotoluene at 130–140° in the presence of dry ammonia or an amine, piperidine, for example; it separates from glacial acetic acid in yellow crystals and melts at 139–140°.

2:4:4'-*Trinitrostilbene*,  $NO_2 \cdot C_6H_4 \cdot CH:CH \cdot C_6H_3(NO_2)_2$ , results from the condensation of 2:4-dinitrotoluene with *p*-nitrobenzaldehyde; it crystallises from nitrobenzene in felted, lemon-yellow needles and melts at 240°.

2:4:3'-*Trinitrostilbene*, obtained from *m*-nitrobenzaldehyde, crystallises from glacial acetic acid in yellow needles and melts at 183–184°.

G. T. M.

**Fluorene.** AKTIEN GESELLSCHAFT FÜR THEER- & ERDÖL-INDUSTRIE (D.R.-P. 124150).—Fluorene reacts with potassium hydroxide at 280°, yielding a solid *potassium* derivative,  $C_{13}H_9K$ , which is decomposed into its generators by water. This reaction can be employed to separate the hydrocarbon from mixtures containing it.

G. T. M.

**Dimethylaniline Oxide.** By EUGEN BAMBERGER and LEO RUDOLF (*Ber.*, 1902, **35**, 1082–1083).—This substance can be most conveniently prepared by oxidising dimethylaniline with an ice-cold diluted solution of Caro's acid, and "salting out" with sodium sulphate; it is freed from small quantities of the latter by dissolving in alcohol and evaporating in an exhausted receiver over sulphuric acid. It fails to interact additively with hydrogen cyanide to yield dimethylaminobenzonitrile, simply effecting polymerisation of the acid to aminomalononitrile.

W. A. D.

**Arylsulphonimides.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 125390).—The anhydrous metallic derivative of an arylsulphonamide, when treated at 180° with an arylsulphonic chloride, yields the corresponding sulphonimide.

*Di-p-toluenesulphonimide*,  $(C_6H_4Me \cdot SO_2)_2NH$ , obtained from the sodium derivative of *p*-toluenesulphonamide and *p*-toluenesulphonic chloride, is a crystallisable substance, readily soluble in ether or alcohol, but dissolving only sparingly in water.

*Di-o-toluenesulphonimide* and *dibenzenesulphonimide*, produced in a similar manner, separate in needles and in crystalline aggregates respectively.

Mixed sulphonimides containing dissimilar aryl radicles are also readily prepared by the preceding method.

G. T. M.

**Benzylethylaniline.** By GUSTAV SCHULTZ and EBERHARD BOSCH (*Ber.*, 1902, **35**, 1292–1296).—The base boils with partial decomposition at 275–298° under atmospheric pressure, and at 185.5–186.5° under 22 mm. pressure, does not solidify, and has sp. gr. 1.034 at 18.5°. The *picrate* crystallises in short prisms and melts at 114°.

*m*-Nitrobenzylethylaniline,  $C_{15}H_{16}O_2N_2$ , crystallises from alcohol in orange-yellow prisms and melts at  $69^\circ$ ; a small quantity of a nitro-derivative melting at  $67^\circ$  is also produced. The *hydrochloride* crystallises from chloroform and melts at  $186^\circ$ . The *picrate* crystallises in prisms and melts at  $131^\circ$ . On oxidation, the base yields *m*-nitrobenzoic acid.

*m*-Aminobenzylethylaniline,  $C_{15}H_{18}N_2$ , is an oil which boils at  $261\text{--}262^\circ$  under 57—58 mm. pressure. The *hydrochloride* crystallises from a mixture of alcohol and ether and melts at  $188\text{--}190^\circ$ .

*p*-Nitrosobenzylethylaniline,  $C_{15}H_{16}ON_2$ , separates from ether in steel-blue crystals and melts at  $62^\circ$ .

*p*-Aminobenzylethylaniline,  $C_{15}H_{18}N_2$ , boils at  $225^\circ$  under 21 mm. pressure. The *hydrochloride* separates from ether as a white, hygroscopic precipitate. The *oxalate* crystallises from alcohol and melts at  $168\text{--}169^\circ$ . The *benzoyl* derivative crystallises in needles and melts at  $124^\circ$ .

T. M. L.

**Action of Cyanogen Bromide on Tertiary Amines. IV.** By JULIUS VON BRAUN and RUDOLF SCHWARZ (*Ber.*, 1902, 35, 1279—1288. Compare *Abstr.*, 1900, i, 430, 641, 687).—*Benzylidipropylamine*,  $C_6H_5\cdot CH_2\cdot NPr_2$ , prepared by heating benzyl chloride and dipropylamine at  $120^\circ$ , is a colourless, odourless oil and boils at  $235\text{--}243^\circ$ . The *hydrochloride* melts at  $156^\circ$ . The *platinichloride* is a reddish-yellow salt and melts at  $156^\circ$ . The *picrate* melts at  $121^\circ$ . By the action of cyanogen bromide, the base is converted into dipropylcyanamide and benzyl bromide.

*Benzylisopropylaniline*,  $C_6H_5\cdot CH_2\cdot NPhPr^s$ , from benzyl chloride and isopropylaniline, boils at  $177\text{--}178^\circ$  under 12 mm. pressure. The *hydrochloride* melts at  $184^\circ$ . The *platinichloride* separates from alcohol in reddish-yellow crystals and melts at  $186^\circ$ . The *picrate* crystallises from a mixture of alcohol and ether and melts at  $138\text{--}140^\circ$ . The base does not react with cyanogen bromide at atmospheric temperatures; at  $100^\circ$ , benzyl bromide, benzylisopropylaniline hydrobromide, and resin are formed. Benzyl-diethylamine behaves similarly, benzyl bromide being formed and the diethylcyanamide being decomposed into diethylamine. Benzylmethylaniline gave benzyl bromide and phenylmethylcyanamide.

Benzylallylaniline interacts with cyanogen bromide to form allyl bromide and *phenylbenzylcyanamide*,  $C_6H_5\cdot CH_2\cdot NPh\cdot CN$ , which boils at  $185\text{--}195^\circ$  under 12 mm. pressure, crystallises from a mixture of alcohol and ether, and melts at  $60^\circ$ ; with ammonia and hydrogen sulphide, it gives phenylbenzylthiocarbamide.

*Dibenzylallylamine*,  $C_8H_9\cdot N(CH_2Ph)_2$ , from allyl iodide and dibenzylamine, is a colourless, odourless oil and boils at  $168\text{--}170^\circ$  under 10 mm. pressure; the *hydriodide* crystallises from a mixture of alcohol and ether, melts at  $210^\circ$ , and is not readily soluble in cold water; the *hydrochloride* melts at  $259^\circ$ ; the *platinichloride* melts at  $168\text{--}169^\circ$ ; the *picrate* was only obtained as an oil. With cyanogen bromide, the base gave dibenzylallylamine *hydrobromide*, which softens at  $210^\circ$  and melts at  $227^\circ$ , and dibenzylcyanamide.

It appears, therefore, that the benzyl radicle is split off more

readily than methyl, ethyl, or phenyl, but less readily than the allyl radicle. T. M. L.

**Phenolic Sulphurous Esters.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 115335. Compare Abstr., 1901, i, 695, and this vol., i, 91).—Resorcinol, 1:8-dihydroxynaphthalene,  $\alpha$ -naphtholsulphonic acids (except the 2- and 3-sulphonic acids or the disulphonic acids derived from them),  $\beta$ -naphtholsulphonic acids (except the 4-sulphonic acid and its derivatives), and 8-amino- $\alpha$ -naphthol-6-sulphonic acid, when heated with a strong solution of sodium hydrogen sulphite (40° Bé) are converted into readily soluble sulphurous esters.

The esters may also be obtained by the action of sodium hydrogen sulphite from the corresponding amino-compounds; they are hydrolysed by alkalis, yielding the phenols, and when treated with ammonia give rise to amines. Hence they may be employed either in converting amino-compounds into phenols, or in bringing about the opposite change by the replacement of hydroxyl by amidogen. G. T. M.

**Phenolic Sulphurous Esters.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 126136. Compare Abstr., 1901, i, 695, and preceding abstract).—Sodium  $\beta$ -naphthylamine-6-sulphonate and 5-hydroxy- $\beta$ -naphthylamine-7-sulphonic acid, when heated with a large excess of sodium hydrogen sulphite solution, yield the sulphurous esters of  $\beta$ -naphthol-6-sulphonic acid and 2:5-dihydroxynaphthalene-7-sulphonic acid respectively. *m*-Phenylenediamine, when treated with the sulphite solution, gives rise to a sulphurous ester of *m*-aminophenol. G. T. M.

[4-Nitro-*p*-hydroxyphenyl- $\alpha$ -naphthylamine.] CHEMISCHE FABRIK VORM. SANDOZ (D.R.-P. 123922).—1-Chloro-4-nitronaphthalene derivatives readily condense with the amino-*p*-phenol or its sulphonic acid, forming 4-nitrophenyl- $\alpha$ -naphthylamine derivatives. These nitro-amino-compounds, when heated with alkali polysulphides, yield colouring matters containing sulphur.

4:8-Dinitro-*p*-hydroxyphenyl- $\alpha$ -naphthylamine, prepared by heating together 4:8-dinitro-1-chloronaphthalene, *p*-aminophenol, and sodium acetate in alcoholic solution at 120—140°, is precipitated by acids from the product as a reddish-brown powder; it crystallises from most organic solvents in needles insoluble in water. The sulphonated derivatives of this compound are obtained in a similar manner. G. T. M.

**Sulphonic Acids of  $\alpha$ -Naphthalenoid Thiocarbamides containing Free Hydroxyl Groups.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 123886).— $\alpha$ -Thiocarbamides of the type  $\text{CS}[\text{NH}\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{SO}_3\text{H}]_2$  are readily obtained by condensing a mixture of two aminonaphtholsulphonic acids with carbon disulphide and sulphur in alcoholic solution (compare this vol., i, 22). G. T. M.

**Benzoylbenzylcarbamide, Benzoyl-*p*-tolylcarbamide, and the Corresponding Ethyl- $\psi$ -carbamides: a Correction.** By HENRY L. WHEELER and TREAT B. JOHNSON (*Amer. Chem. J.*, 1902, 27, 218—219).—Re-examination of the substances previously described



(Abstr., 1900, i, 633—634) as benzoylbenzylcarbamide and benzoyl-*p*-tolylcarbamide, melting at 89° and 80° respectively, has shown that they are not normal but  $\psi$ -carbamides.

*Benzoylbenzylethyl- $\psi$ -carbamide* (previously described as benzoylbenzylcarbamide), crystallises from alcohol in colourless prisms and melts at 89—90°; it is converted by hydrochloric acid into ethyl chloride and the true *benzoylbenzylcarbamide*, which forms colourless prisms and melts at 165—166°.

*Benzoyl-*p*-tolylethyl- $\psi$ -carbamide* crystallises from alcohol in colourless prisms and melts at 75°; when treated with hydrochloric acid, it yields ethyl chloride and the true *benzoyl-*p*-tolylcarbamide*, which crystallises in needles and melts at 222—223°. E. G.

**Phenylglycine-*o*-carboxylic Acid.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 125456. Compare Abstr., 1901, i, 710).—Phenylglycine-*o*-carboxylic acid is prepared by heating together at 220° the sodium salts of glycine and *o*-chlorobenzoic acid or its bromine analogue. G. T. M.

**Action of Oxidising Agents on Pentachlorophenol.** By ETIENNE BARRAL (*Bull. Soc. Chim.*, 1902, [iii], 27, 271—275).—By the action of certain oxidising agents, such as nitric acid, on pentachlorophenol, tetrachloroquinone is formed, although the conversion is in no case complete, whilst in many cases, as with chromic acid or permanganate, it is not produced. A. F.

**Transformation of Pentachlorophenol into Tetrachloroquinone.** By ETIENNE BARRAL (*Bull. Soc. Chim.*, 1902, [iii], 27, 275—278. Compare preceding abstract).—By the action of chlorine on pentachlorophenol, heptachlorophenol is produced, and this, on heating, decomposes into hexachlorophenol and hydrogen chloride; hexachlorophenol, when acted on by oxidising agents, yields tetrachloroquinone. Since in those cases where tetrachloroquinone is produced by the action of oxidising agents on pentachlorophenol chlorine is formed, the author considers that in such cases the formation of tetrachloroquinone is due to the intermediate formation of heptachlorophenol and hexachlorophenol. A. F.

**Behaviour of Picric Acid towards boiling Alkali Hydroxides.** By EDGAR WEDEKIND and J. HAEUSSERMANN (*Ber.*, 1902, 35, 1133—1135).—On boiling picric acid with excess of potassium, sodium, or barium hydroxide, ammonia is slowly evolved; after 8 hours, the evolution ceases. Approximately 5·9 per cent. of ammonia is given off, whilst 1NH<sub>3</sub> requires 7·8 per cent. Prussic acid can be detected in the alkaline mother liquor together with nitrite. The amount of the latter is quantitatively different with the three alkali hydroxides; thus, from 1 gram of picric acid was obtained, with potassium hydroxide, 36·4 mg. of nitric oxide; with sodium hydroxide, 57·4 mg., and with barium hydroxide, 79·8 mg. respectively. No solid products of the reaction were isolated. K. J. P. O.

**Preparation of Thymol.** M. DINESMANN (D.R.-P. 125097).—2-Bromo-*p*-cymene, when treated with fuming sulphuric acid, yields a monosulphonic acid, which, on heating with zinc dust and ammonia at 170°, gives rise to a cymenesulphonic acid. This reduction product, when fused with potassium hydroxide, furnishes thymol. G. T. M.

**"Halochromy" of 2:7-Dimethoxynaphthalene.** By HUGO KAUFFMANN (*Ber.*, 1902, 35, 1321—1324. Compare Abstr., 1900, i, 480; 1901, i, 318; and also Baeyer and Villiger, this vol., i, 380).—Dimethoxynaphthalene, when quite pure, is obtained in perfectly colourless crystals; its solution in concentrated sulphuric acid is yellow and has a well-marked, green fluorescence. A 1 per cent. solution of the ether in the concentrated acid has a reddish-brown colour similar to that of potassium dichromate, but the fluorescence is less appreciable than in more dilute solutions. These appearances are not due to a decomposition of the substance, for it is obtained quite colourless by diluting the solution with ice-cold water; the addition of glacial acetic acid, alcohol, or ether always destroys both the coloration and the fluorescence. Concentrated hydrochloric and phosphoric acids, when employed separately, do not develop any coloration with the ether, but a solution of the substance in syrupy phosphoric acid, when treated with hydrogen chloride, exhibits the same colour and fluorescence as when concentrated sulphuric acid is the solvent. The ether also exhibits intense luminescence under the influence of the Tesla radiations, and these phenomena are probably due to a tendency for the formation of a quinonoid structure in the substance under examination.

G. T. M.

**The so-called Dinaphthylene Glycol.** By ROBERT FOSSE (*Compt. rend.*, 1902, 134, 663—664. Compare Abstr., 1901, i, 322, 384, 643, and this vol., i, 51, 171).—As already indicated, the supposed dinaphthylene glycol is in reality dinaphthaxanthhydrol. This view of the constitution of the substance is confirmed by the formation of the *acetyl* derivative,  $\text{OAc} \cdot \text{CH} \begin{smallmatrix} \text{C}_{10}\text{H}_6 \\ \text{C}_{10}\text{H}_6 \end{smallmatrix} \text{O}$ , by the action of acetic anhydride either on the compound itself or its anhydride, the product melting at 194°. Fuming hydrobromic acid converts the hydrol or its anhydride into bromodinaphthaxanthen, to which the constitution  $\text{CH} \begin{smallmatrix} \text{C}_{10}\text{H}_6 \\ \text{C}_{10}\text{H}_6 \end{smallmatrix} \text{O} \cdot \text{Br}$  is now given; this product, when treated with alcohol, oxidises the latter to aldehyde and loses hydrogen bromide, becoming itself converted into dinaphthaxanthen.

G. T. M.

**Solubility of Silver Benzoate.** By CARL LIEBERMANN (*Ber.*, 1902, 35, 1094).—Silver benzoate is erroneously stated in many handbooks to be soluble in 1.96 parts of absolute alcohol at 20°; this solubility is really that of benzoic acid, the silver salt being soluble only in 5910 parts of cold, and in 2150 parts of hot, alcohol.

W. A. D.

**Formation, Decomposition, and Germicidal Action of Benzoyl Acetyl and Diacetyl Peroxides.** By PAUL C. FREER and FREDERICK G. NOVY (*Amer. Chem. J.*, 1902, 27, 161—192).—The

conditions under which benzylidene diacetate is produced by the action of acetic anhydride on benzaldehyde were investigated. The rate of action is increased by the presence of traces of acetic acid, but appears to be diminished if a large quantity is present. Metals such as platinum, zinc, tin, and iron cause a considerable acceleration. If air is passed through a carefully dried mixture of benzaldehyde and acetic anhydride, the formation of the diacetate is retarded, and benzoic acetic peroxide is produced in quantities large enough to admit of estimation.

When a solution of benzoic acetic peroxide (2 mols.) in benzaldehyde is heated, decomposition occurs with formation of carbon dioxide (2 mols.) and methane (1 mol.). This decomposition was employed for the estimation of the benzoic acetic peroxide produced in the following experiments.

Dry air was passed through a series of tubes containing a dry mixture of acetic anhydride and benzaldehyde; the amount of peroxide produced was very small, but in presence of small pieces of certain metals (particularly magnesium) or filter paper the quantity was considerably increased. The results of these experiments show that the rate of formation of the peroxide depends on the surface action of substances coming in contact simultaneously with air and the mixture of acetic anhydride and benzaldehyde; the presence of moisture is not necessary. The probable course of the reaction is discussed, and the best method of preparing the peroxide described.

Benzoic acetic peroxide melts at 40—41°. It reacts with aniline with formation of acetanilide, azoxybenzene, benzoic acid, and traces of perbenzoic acid,  $C_6H_5 \cdot CO \cdot O \cdot OH$ . It also reacts slowly with quinol with production of quinhedrone; this action is probably due to the presence of traces of water. Although the solid peroxide does not exert an oxidising action, its aqueous solution liberates iodine from potassium iodide. This difference in behaviour was found to be due to hydrolysis, the rate of which was estimated; the results are tabulated. The hydrolysed solution yields an insoluble precipitate of benzoic peroxide and a clear liquid containing acetic and benzoic acids, peracetic acid, and some perbenzoic acid. The solubility of the peroxide at 25° was determined; in five minutes, an amount corresponding with 0.639 gram per litre was dissolved. By the action of sodium ethoxide on benzoic acetic peroxide, benzoic acid and perbenzoic acid are produced.

When acetic peroxide is treated at -20° with sodium ethoxide, a white, unstable salt is produced which, when treated with frozen dilute sulphuric acid, yields an oil with an odour resembling that of chlorine oxides; this substance, which is undoubtedly peracetic acid, rapidly undergoes decomposition. Acetic peroxide, unlike benzoic acetic peroxide, when left in contact with water slowly evolves oxygen. The hydrolysis of the solution is complete in a few minutes.

The action of the peroxides on various bacterial cultures was studied; the results are tabulated. Benzoic peroxide does not exert any germicidal action, owing to the fact that it does not undergo hydrolysis in solution; the hydrolysed solutions of acetic peroxide and benzoic acetic peroxide, however, exhibit a remarkable germicidal

effect. The results show that whilst the symmetrical organic peroxides are inert, the unsymmetrical per-acids are amongst the most powerful germicidal agents known.

E. G.

**Esterification of Acids with Phenols.** By MARUSSIA BAKUNIN (*Gazzetta*, 1902, **34**, i, 178—185).—The author has studied the preparation of the phenylnitrocinnamates and phenylcinnamates of mono-, di-, and tri-hydric phenols by the action of phosphoric oxide on the acid and phenol dissolved in a neutral solvent. As the energy of the reaction increases with the number of hydroxyl groups in the phenol, a solvent of high boiling point, such as toluene, should be employed in the case of di- and tri-hydric phenols. When the latter are used in excess, they yield only mono-substituted derivatives.

*o*-Tolyl phenyl-*o*-nitrocinnamate,  $C_{15}H_{10}O_3N \cdot O \cdot C_6H_4Me$ , separates from alcohol in yellow, apparently rhomboidal, prisms melting at 97—98°.

*o*-Tolyl phenyl-*m*-nitrocinnamate is deposited from alcohol in crystalline granules melting at 118—120°.

*o*-Tolyl allophenyl-*m*-nitrocinnamate crystallises from alcohol in tufts of silky, white needles melting at 83—84°.

*o*-Tolyl phenyl-*p*-nitrocinnamate separates from alcohol in pale yellow needles melting at 128—129°.

*o*-Tolyl allophenyl-*p*-nitrocinnamate, which is obtained mixed with small quantities of phenylnitroindone, crystallised from alcohol in straw-yellow needles melting at 120°.

*o*-Tolyl phenylcinnamate,  $C_{15}H_{11}O \cdot O \cdot C_6H_4Me$ , separates from alcohol in silky needles melting at 130°.

2-Methyl-5-isopropylphenyl phenylcinnamate,  $C_{15}H_{11}O \cdot O \cdot C_6H_3MePr^s$ , is deposited from alcohol in bristly needles having a silky lustre and melting at 80—81°.

*m*-Hydroxyphenyl phenylcinnamate,  $C_{15}H_{11}O \cdot O \cdot C_6H_4 \cdot OH$ , crystallises from alcohol in silky needles melting at 157—160°.

*m*-Phenylene diphenylcinnamate,  $C_6H_4(C_{15}H_{11}O_2)_2$ , obtained in small quantity mixed with the preceding compound, separates from alcohol in granules melting at 162°.

*o*-Phenylene phenylcinnamate is deposited from benzene in needles melting at 169°.

*p*-Phenylene phenylcinnamate crystallises from benzene in silky needles melting at 126—127°, and is accompanied by small quantities of a substance soluble in sodium carbonate solution and melting at 160°.

Pyrogallol phenylcinnamate,  $C_{15}H_{11}O \cdot O \cdot C_6H_3(OH)_2$ , separates from benzene in flocks of white needles melting at 159°.

T. H. P.

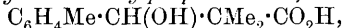
**Glyceryl Salicylate.** ERNST TÄUBER (D.R.-P., 126311).—*Glyceryl salicylate*,  $OH \cdot C_6H_4 \cdot CO_2 \cdot C_3H_5(OH)_2$ , produced by heating salicylic acid with excess of glycerol in the presence of a small quantity of 60 per cent. sulphuric acid, melts at 76°, and although sparingly soluble in cold dissolves readily in hot water. The ester is odourless, readily soluble in most organic solvents, and miscible with glycerol; it forms a compound with calcium chloride, and is readily hydrolysed by alkali hydroxides and carbonates.

G. T. M.

**Synthesis of  $\beta$ -Hydroxy- $\beta$ -*p*-tolyl- $\alpha$ -dimethylpropionic Acid.**

By I. ZELTNER (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 119—128).—The action of zinc on a mixture of ethyl bromoisobutyrate and *p*-methylbenzaldehyde gives rise to ethyl  $\beta$ -hydroxy- $\beta$ -*p*-tolyl- $\alpha$ -dimethylpropionate according to the equations: (1)  $\text{CMe}_3\text{Br}\cdot\text{CO}_2\text{Et} + \text{Zn} = \text{ZnBr}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ ; (2)  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHO} + \text{ZnBr}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et} = \text{C}_6\text{H}_4\text{Me}\cdot\text{CH}(\text{OZnBr})\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ ;  
 (3)  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}(\text{OZnBr})\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et} + \text{H}_2\text{O} = \text{C}_6\text{H}_4\text{Me}\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et} + \text{Zn}(\text{OH})\text{Br}$ .

*$\beta$ -Hydroxy- $\beta$ -*p*-tolyl- $\alpha$ -dimethylpropionic acid,*



crystallises from alcohol in small prismatic needles melting at 111.5—112.5; it is soluble in water and slightly volatile in a current of steam, and gives the normal molecular weight in boiling ether. The *potassium* and *barium* salts were analysed and the *zinc*, *lead*, *nickel*, *cobalt*, *iron*, *mercury*, *silver*, and *copper* salts prepared. The *ethyl* ester is a slightly yellow, very viscous liquid boiling at 172—173° under 15 mm. pressure and having the normal molecular weight in boiling ether;  $n_D$  1.50439 at 19°. When heated with dilute sulphuric acid, the acid is decomposed partly into carbon dioxide, water, and *isobutenyltoluene*, and partly into *isobutyric* acid and *p*-methylbenzoic acid. Heating the acid under pressure with concentrated hydriodic acid also gives rise to *isobutenyltoluene*, which is further obtained, together with *p*-methylbenzaldehyde, when the acid is submitted to dry distillation.

The acid is not obtained if the zinc be replaced by magnesium, as in this case a compound,  $\text{C}_{11}\text{H}_{14}\text{O}_2$ , separating from ether in crystals melting at 138—139° is formed, together with *p*-methylbenzaldehyde.

T. H. P.

**Action of Formaldehyde on *o*-Aminobenzoic Acid in Hydrochloric Acid Solution.** By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1902, **26**, 179—180).—The amorphous substances obtained by Mehner (*Abstr.*, 1901, i, 470) by the action of formaldehyde on hydrochloric acid solutions of *o*-aminobenzoic acid and methyl *o*-aminobenzoate respectively have been examined. From the acid, a substance of the formula  $\text{O}(\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$ , is formed, and from the ester a compound,  $\text{CH}_2\text{Cl}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ . These substances possess anti-septic properties.

J. McC.

**Polymerised Condition of ordinary Indigotin and the Transformation of Indigotin into Indirubin.** By LOUIS MAILLARD (*Compt. rend.*, 1902, **134**, 470—472. Compare *Abstr.*, 1901, ii, 407).—A mixture of indoxyl sulphate, chloroform, and concentrated hydrochloric acid develops a deep blue coloration which is far more intense than that of a saturated chloroform solution of crystallised indigotin. If the mixture is at once washed with dilute sodium hydroxide solution, the chloroform extract yields a precipitate of ordinary indigotin; but when it is allowed to remain in the presence of the acid, no precipitation occurs, the colour, however, becomes violet and finally red, and the

chloroform extract on evaporation leaves a residue of indirubin. A similar phenomenon is observed when urine is treated with hydrochloric acid containing a little ferric chloride. In both cases, the "nascent" indigotin produced from the indoxyl by atmospheric oxidation appears to be far more soluble in chloroform than the crystallised variety, and changes into indirubin when allowed to remain in contact with the acid. This transformation never occurs with a solution of the crystallised substance. This difference is in all probability due to polymerisation, the "nascent" variety of indigotin having the simple indigo formula  $C_{16}H_{10}O_2N_2$ , whilst the crystallised modification is *bis-indigotin*,  $C_{32}H_{20}O_4N_4$ . This view of the molecular complexity of crystalline indigotin is confirmed by Vaubel, who found that the molecular weights of indigotin and indirubin determined by the cryoscopic method in phenol and *p*-toluidine solutions correspond with the dimeric formulæ. The "nascent" variety of indirubin has not yet been isolated. Chloroform solutions of the ordinary modification, *bis-indirubin*, in the presence of alkali hydroxides do not give rise to any trace of indigotin; it is, however, quite possible that the inverse transformation might occur with the monomeric indirubin.

G. T. M.

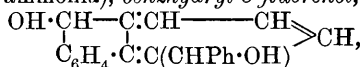
**Action of Phosphorus Pentachloride on Tetrachloro-*o*-benzoylbenzoic Acid.** By LÉON TÉTRY (*Bull. Soc. Chim.*, 1902, [iii], 27, 183—186).—On heating tetrachloro-*o*-benzoylbenzoic acid with phosphorus pentachloride in a sealed tube at 140—150° for 5 hours, as described by Kircher (*Abstr.*, 1887, 831), the author obtained, not only tetrachloro-*o*-benzoylbenzoic chloride, but also, as the principal product, *ω*-dichloro-*o*-benzyltetrachlorobenzoic chloride,  $CPhCl_2 \cdot C_6Cl_4 \cdot COCl$ , a white, crystalline substance which melts at 143—144° and is readily soluble in benzene, toluene, or chloroform, but insoluble in alcohol. Cold concentrated sulphuric acid has no action on it, but the hot acid decomposes it with evolution of hydrogen chloride and production of a red coloration. The author has improved the yield of *o*-benzoyltetrachlorobenzoic chloride by heating *o*-benzoyl tetrachlorobenzoic acid with phosphorus pentachloride dissolved in carbon disulphide at a temperature of 30—40°.

A. F.

**Condensation of Diphenic Anhydride with Benzene.** By RUDOLF GÖTZ (*Monatsh.*, 1902, 23, 27—43).—On boiling a solution of diphenic anhydride in benzene with excess of aluminium chloride, 50 per cent. of *diphenyleneketonecarboxylic acid* (*fluorenone-5-carboxylic acid*),  $\begin{array}{c} CO-CH \\ | \quad | \\ C_6H_4 \cdot C(CO_2H) \cdot CH \end{array}$ , and 10—15 per cent. of *benzoyl-5-fluorenone*,  $\begin{array}{c} CO-CH \\ | \quad | \\ C_6H_4 \cdot C(COPh) \cdot CH \end{array}$ , are produced (compare Graebe and Aubin, *Abstr.*, 1889, 145); the acid crystallises in yellow needles melting at 227°. By thionyl chloride, it is converted into *fluorenone-5-carboxylic chloride*,  $C_{13}H_7O \cdot COCl$ , which crystallises in long, yellow needles melting at 128°. Benzoyl-5-fluorenone, obtained as just described or by the action of aluminium chloride and benzene on

fluorenone-5-carboxylic chloride, forms amber-yellow, prismatic crystals melting at 95° and boiling above 400°. The *dioxime* forms crystals melting at 215°; the *monoxime* crystals melting at 146°; the *acetyl* derivative of the latter forms small crystals melting and decomposing at 130°. The *monophenylhydrazone* of benzoyl-5-fluorenone,  $C_{26}H_{18}ON_2$ , crystallises in yellow needles melting at 171—173°.

On distilling benzoylfluorenone with zinc dust in a current of hydrogen, *benzyl-5-fluorene*,  $\begin{array}{c} CH_2-C:CH-CH \\ | \quad | \quad | \\ C_6H_4 \cdot C:C(CH_2Ph) \cdot CH \end{array}$  is obtained, which crystallises in lustrous leaflets melting at 77°. When benzoylfluorenone is reduced with sodium amalgam and alcohol, or by zinc dust and acetic acid (or alcoholic ammonia), *benzhydryl-5-fluorene*,



is formed; it crystallises in white needles melting at 145° and dissolves in concentrated sulphuric acid with an emerald green colour; the *diacetate* forms needles melting at 126°.

On reducing benzoylfluorenone with a small quantity of sodium amalgam, or by oxidising benzhydrylfluoreneol with potassium permanganate, a substance is obtained which is either *benzoylfluoreneol* or *benzhydrylfluoreneol*; it crystallises in small, sulphur-yellow scales melting at 129°, and dissolves in concentrated sulphuric acid with a reddish-green fluorescence; the *acetate*,  $C_{20}H_{13}O_2 \cdot OAc$ , forms pale yellow needles melting at 121°; the *phenylhydrazone*,  $C_{20}H_{14}O \cdot N_2HPh$ , yellow crystals melting and decomposing at 194°. K. J. P. O.

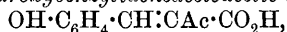
**Salicylglycollic Acid.** KNOLL & Co. (D.R.-P. 125988 and 125989).—Ethyl salicylglycollate (Senff, Abstr., 1881, 1127), prepared by heating sodium salicylate with ethyl chloroacetate, is readily hydrolysed by cold 25 per cent. sodium hydroxide solution by boiling for 24 hours with 50 per cent. acetic acid or by digestion at 40° with 80 per cent. sulphuric acid or 25 per cent. hydrochloric acid. *Salicylglycollic acid* crystallises from chloroform or benzene in prisms or leaflets melting at 132°; it develops a reddish-violet coloration with ferric chloride. The acid yields salicylic acid by artificial digestion or on treatment with warm solutions of the alkali hydroxides, but is not affected by gastric juice. The *sodium hydrogen* salt crystallises in needles melting at 203°; the *sodium* salt decomposes at 260°. The salts of the heavy metals are insoluble; those of calcium, strontium, and barium crystallise in needles. G. T. M.

**Condensation Products from Aromatic Aldehydes and Malononitrile.** By WILHELM WALTER (*Ber.*, 1902, 35, 1320—1321).—*p*-Dimethylaminobenzylidenemalononitrile,  $NMe_2 \cdot C_6H_4 \cdot CH:C(CN)_2$ , produced by condensing *p*-dimethylaminobenzaldehyde with malononitrile in alcohol containing a small quantity of sodium carbonate, crystallises in orange-coloured needles and melts at 179°.

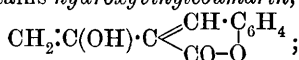
2:4-Dihydroxybenzylidenemalononitrile,  $C_6H_3(OH)_2 \cdot CH:C(CN)_2$ , obtained in a similar manner from resorcinolaldehyde, is sparingly soluble in alcohol or glacial acetic acid, yielding a yellow solution with a green fluorescence; it is a yellow-brown substance melting above 300°.

*Isatomalononitrile*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{C}:\text{C}(\text{CN})_2$ , obtained by mixing isatin and malononitrile in alcoholic solution, crystallises in yellowish-brown, felted needles and melts at  $235^\circ$ ; it is soluble in hot water, alcohol, ether, benzene, or glacial acetic acid; with sodium hydroxide solution, a blue coloration is developed, and finally a yellow solution is obtained. G. T. M.

**Desmotropy between Acetyl and Hydroxyvinyl Groups.** By OSKAR WIDMAN (*Ber.*, 1902, 35, 1153—1159).—Acetylcoumarin,  $\text{C}(\text{Ac})=\text{CH}\cdot\text{C}_6\text{H}_4$  (Knoevenagel and Amot, *Abstr.*, 1898, i, 406), dissolves in cold *N/10* sodium hydroxide, forming a deep yellow solution, which on heating becomes much paler in tint. The latter, less coloured, solution contains *o*-hydroxybenzylideneacetoacetic acid,



which can be isolated in an impure state and begins to decompose at  $118^\circ$ , but is not completely melted at  $160$ — $170^\circ$ . The deep yellow alkaline solution contains *hydroxyvinylcoumarin*,



on acidification, no immediate precipitation occurs, but acetylcoumarin slowly separates as the hydroxyvinyl compound gradually undergoes isomeric change and the solution becomes neutral. Strong acids bring about an immediate separation of acetylcoumarin. The hydroxyvinyl compound can be extracted with ease by means of ether, in which it is very soluble, whereas acetylcoumarin does not dissolve particularly readily in that solvent; on the other hand, chloroform extracts the hydroxyvinyl compound from water only slowly, whilst it dissolves the acetyl derivative with great ease. With ferric chloride, an ethereal solution of hydroxyvinylcoumarin gives a yellowish-brown coloration; acetylcoumarin in ethereal solution gives no such colour. On passing dry ammonia into a solution of hydroxyvinylcoumarin in anhydrous ether or chloroform, the ammonium salt is immediately precipitated. Acetylcoumarin, when similarly treated, gives no ammonium derivative.

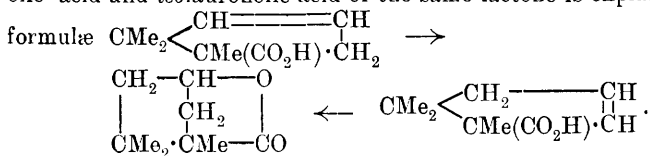
It is pointed out that the yellow, insoluble barium salt of acetylacrylic acid, described by Wolff (*Abstr.*, 1891, 1185), is the salt of a hydroxyvinylacrylic acid,  $\text{CH}=\text{C}(\text{CH}_2\text{O})\cdot\text{CO}\cdot\text{O} \cdot \text{Ba}$ . The author finds that various ethyl alkylideneacetoacetates, on treatment with alkalis, similarly give yellow solutions, which, in the author's opinion, contain hydroxyvinyl derivatives. K. J. P. O.

**Isomeric Dehydrocamphoric and Lauronolic Acids and Dihydrolauro lactone.** By JULIUS BREDT, JOS. HOUBEN, and PAUL LEVY (*Ber.*, 1902, 35, 1286—1292).—Dehydrocamphoric acid (*Annalen*, 1898, 299, 138),  $\text{CMe}_2 \begin{smallmatrix} \text{C}(\text{CO}_2\text{H})=\text{CH} \\ \diagdown \quad \diagup \\ \text{CMe}(\text{CO}_2\text{H})\cdot\text{CH}_2 \end{smallmatrix}$ , melts at  $202$ — $203^\circ$  and does not form an anhydride. When distilled, it is partially converted into the anhydride of an *isodehydrocamphoric acid*, probably



$\text{CMe}_2 \begin{matrix} \text{CH}(\text{CO}_2\text{H})-\text{CH} \\ \text{CMe}(\text{CO}_2\text{H}) \cdot \text{CH} \end{matrix}$ , which melts at  $178-179^\circ$ , whilst the anhydride melts at  $182-183^\circ$ . Lauronolic acid is also formed, and both the dehydrocamphoric acid and the lauronolic acid are oxidised to camphoronic acid.

The formation and reactions of these compounds are in accordance with Bredt's formula for camphor, whilst the formation from lauronolic acid and *isolauronolic* acid of the same lactone is explained by the formulæ



T. M. L.

**Hydramides and their Reactions with Ethyl Cyanoacetate.** By LODOVICO BECCARI (*Atti R. Accad. Sci. Torino*, 1902, **37**, 137—166).—After giving an historical account of the chemistry of the hydramides, the author gives the results of his own investigations on the reactions taking place between these substances and ethyl cyanoacetate. When these compounds are mixed in alcoholic solution in the cold, the liquid turns yellow more or less rapidly, ammonia being evolved and crystalline products formed. The nature of the latter varies in any particular case with the ratio between the amounts of hydramide and ethyl cyanoacetate employed, but the reaction always corresponds with a general scheme according to which the methylenic hydrogen of the cyanoacetate combines with either all or only part of the nitrogen, the residues then combining. In some cases, the structure of the hydramide molecule appears to be preserved, whilst in others it is destroyed.

The compound obtained by the interaction of hydrobenzamide (1 mol.) and ethyl cyanoacetate (2 mols.) has the constitution  $\text{CHPh} \cdot \text{N} \cdot \text{CHPh} \cdot \text{C}(\text{CN})(\text{CO}_2\text{Et}) \cdot \text{CHPh} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , and separates from a mixture of alcohol and benzene in colourless, shining, prismatic crystals which melt and decompose at  $197^\circ$  and are readily soluble in benzene, less so in alcohol or ether, and insoluble in water or dilute acids or alkalis; it has a neutral reaction and gives the normal mol. weight in freezing benzene. When heated carefully at temperatures below  $200^\circ$ , it yields small quantities of ammonia together with ethyl  $\alpha$ -cyano- $\beta$ -phenylacrylate. It is very resistant to the action of alkalis and acids; heating with 60 per cent. potassium hydroxide solution decomposes it, but it is not attacked by boiling with concentrated hydrochloric acid; 50 per cent. sulphuric acid is without action on it, but by 70 per cent. acid it is completely decomposed into benzaldehyde, ammonia, and carbon dioxide.

The action of excess of ethyl cyanoacetate on hydrobenzamide results in the formation of the compound  $\text{C}_{22}\text{H}_{19}\text{O}_3\text{N}_3$ , obtained by Carrick (*Abstr.*, 1892, 1086) by the interaction of alcoholic ammonia and ethyl  $\alpha$ -cyanophenylacrylate (see also Bertini, *Abstr.*, 1901, i, 537).

Anishydramide (*p*-methoxybenzhydramide) (1 mol.) and ethyl cyano-

acetate (2 mols.) yield a compound,  $C_{34}H_{35}O_7N_3$ , which has a structure analogous to that already given, and separates from alcohol in white, acicular crystals melting and decomposing at  $174^\circ$ ; it is readily soluble in benzene, to which it gives the normal depression of freezing point. If the ethyl cyanoacetate is used in excess (4 mols.), the anishydramide molecule undergoes decomposition with the formation of ammonia and ethyl *p*-methoxyphenyl- $\alpha$ -cyanoacrylate.

Furfuramide (furfurylhydramide) (1 mol.) reacts with ethyl cyanoacetate (2 mols.), yielding ethyl furfuryl- $\alpha$ -cyanoacrylate, which is also formed when the cyanoacetate is used in excess.

The interaction of salicylhydramide (*o*-hydroxybenzhydramide) and ethyl cyanoacetate yields ethyl *o*-hydroxybenzylidenedicyanoacetate and a small quantity of another compound not yet investigated.

The final action of ethyl cyanoacetate on the hydramides, which proceeds to completion in some cases, may be represented as follows:

$$\begin{array}{c} R':N \\ R'':N \end{array} > R'' + 3 \begin{array}{c} H \\ H \end{array} C \begin{array}{l} \swarrow CN \\ \searrow CO_2Et \end{array} = 3 R':C \begin{array}{l} \swarrow CN \\ \searrow CO_2Et \end{array} + 2NH_3; \text{ the compounds obtained from hydrobenzamide, \&c., must be regarded as due to a partial scission of the hydramide, only part of the nitrogen being eliminated in the form of ammonia and replaced by one or more cyanoacetic radicles.}$$

T. H. P.

**Isolation of Aldehydes.** CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 124229).—When a liquid containing an aldehyde is treated with a 10 per cent. solution of the barium salt of an aromatic amino-carboxylic or aminosulphonic acid, an insoluble compound is formed which on subsequent distillation in steam regenerates the aldehyde. Benzaldehyde and its homologues and derivatives, cinnamaldehyde, citral, citronellal, and salicylaldehyde may be isolated by this method. The insoluble compounds are obtained with the barium salts of naphthionic, sulphanilic, *m*-aminobenzoic, 2-hydroxy- $\alpha$ -naphthylamine-3-carboxylic, and  $\alpha$ -naphthylamine-5-sulphonic acids.

G. T. M.

**2:4-Dinitrobenzaldehyde.** By PAUL COHN and PAUL FRIEDLÄNDER (*Ber.*, 1902, 35, 1265—1267).—2:4-Dinitrobenzyl chloride, obtained in a nearly theoretical yield by nitrating benzyl chloride, crystallises from ether in large yellow plates, melts at  $34^\circ$ , and is much more sensitive to alkalis than the parent substance. 2:4-Dinitrobenzyl acetate forms yellow, monoclinic plates melting at  $96$ — $97^\circ$ , and 2:4-dinitrobenzyl alcohol lemon-yellow needles melting at  $114$ — $115^\circ$ . 2:4-Dinitrobenzylaniline is orange-red; 2:4-dinitrobenzyl-*p*-toluidine forms slender, red needles melting at  $93^\circ$ ; 2:4-dinitrobenzyl- $\alpha$ -naphthylamine dark red scales melting at  $164^\circ$ , and 2:4-dinitrobenzylaniline-*p*-sulphonic acid brownish-yellow needles.

2:4-Dinitrobenzaldehyde crystallises from a mixture of benzene and light petroleum in lustrous, bright yellow, rhombic plates, melts at  $68$ — $69^\circ$ , and is hardly volatile with steam; on oxidation, it yields 2:4-dinitrobenzoic acid. 2:4-Dinitrobenzylideneaniline forms thick, orange-yellow needles; the analogous derivatives of *p*-toluidine and  $\alpha$ -naphthylamine melt at  $151^\circ$  and  $202^\circ$  respectively. The phenyl-hydrazone of the aldehyde crystallises from xylene in reddish-brown

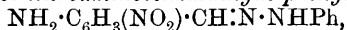
slender needles and melts at 227—228°; the *oxime* separates from water in silky needles, melts at 127—128°, and yields a *benzoyl* derivative crystallising in yellowish needles and melting at 165—166°. 2:4-Dinitrobenzonitrile, obtained by heating the oxime with acetic anhydride, forms brownish-yellow needles, melts at 104—105°, and is transformed by dilute sulphuric acid into dinitrobenzamide.

By the action of light, 2:4-dinitrobenzaldehyde is converted into *o*-nitroso-*p*-nitrobenzoic acid, which melts above 300° and yields a *methyl ester* crystallising in silky, yellow needles and melting at 137—138°.

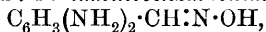
W. A. D.

**New Method of Preparation of Nitrobenzaldehydes.** By FRANZ SACHS and R. KEMPF (*Ber.*, 1902, 35, 1224—1240).—Nitroso-dimethylaniline undergoes condensation with di- and tri-nitrotoluenes, but not with mononitrotoluene, forming a derivative of the corresponding nitrobenzaldehyde. 2:4-Dinitrobenzaldehyde-*p*-dimethylaminoanil,  $C_6H_3(NO_2)_2 \cdot CH:N \cdot C_6H_4 \cdot NMe_2 \cdot H_2O$ , is prepared from nitroso-dimethylaniline and dinitrotoluene in alcoholic solution in presence of sodium carbonate, and crystallises in deep green needles with a metallic lustre which when rapidly heated melt at 193°. The corresponding *diethylaminoanil* melts and decomposes at about 173°. 2:4-Dinitrobenzaldehyde,  $C_6H_3(NO_2)_2 \cdot CHO$ , is obtained by the hydrolysis of the foregoing compounds with dilute nitric acid, and crystallises in long, yellowish needles melting at 72°; it boils at 190—210° under a pressure of 10—20 mm. The *sodium hydrogen sulphite* compound crystallises in stellate groups of slender needles and is readily soluble in water. The *phenylhydrazone* is insoluble in water, crystallises in slender, dendritic needles, and melts at 232° when rapidly heated. The *p*-sulphonic acid of the phenylhydrazone crystallises in slender, reddish-yellow needles, and melts and decomposes at about 217°. 2:4-Dinitrobenzaldehyde *phenylbenzylhydrazone* crystallises in lustrous yellow tablets melting at 155—156°. The *p*-nitro-*phenylhydrazone* melts and decomposes at 283—285°. All these hydrazones undergo hydrolysis with extreme difficulty.

2:4:2':4'-Tetranitrobenzalazine,  $N_2[CH \cdot C_6H_3(NO_2)_2]_2$ , forms long, golden-yellow needles or rhombic crystals and melts at 246°. 2:4-Dinitrobenzylideneaniline,  $C_6H_3(NO_2)_2 \cdot CH:NPh$ , crystallises in light yellow needles melting at 133°. 2:4-Dinitrobenzaldoxime crystallises in long, colourless needles melting at 125°. Nitroaminobenaldoxime,  $NH_2 \cdot C_6H_3(NO_2)_2 \cdot CH:N \cdot OH$ , is prepared by the partial reduction of the oxime with ammonium sulphide and crystallises in matted, orange-yellow needles melting at 177—178°. It is converted by phenylhydrazine into nitroaminobenzaldehyde phenylhydrazone,



which melts at 163°. 2:4-Diaminobenaldoxime,



is obtained by the more complete reduction of the dinitro-compound and crystallises in glistening, white plates melting at about 199—200°; it readily dissolves in dilute acids.

[With W. EVERDING.]—2:4-Dinitrobenzaldehyde may also be prepared from dinitrobenzyl chloride. This is first converted by the action of

aniline into 2:4-dinitrobenzylaniline,  $C_6H_3(NO_2)_2 \cdot CH_2 \cdot NHPh$ , which forms golden-yellow, rectangular tablets melting at  $95^\circ$  (corr.). The hydrochloride melts at  $187^\circ$  (corr.), and the picrate at  $136^\circ$  (corr.). When treated in acetone solution with potassium permanganate, it is converted into 2:4-dinitrobenzylideneaniline, from which the aldehyde is obtained by hydrolysis.

2:4:6-Trinitrobenzaldehyde,  $C_6H_2(NO_2)_3 \cdot CHO$ , is prepared from trinitrotoluene and nitrosodimethylaniline, and crystallises in lancet-shaped needles melting at  $119^\circ$ .

[With HERM. BARSCHALL.]—*p*-Nitrobenzyl chloride condenses with nitrosodiethylaniline to form reddish-brown crystals, melting indefinitely at  $154^\circ$ , the composition of which has not been ascertained. On hydrolysis, this substance yields *p*-nitrobenzaldehyde and diethyl-*p*-phenylenediamine. These two compounds readily form *p*-nitrobenzaldehyde-*p*-diethylaminoanil, which closely resembles the compound just described, but melts at  $142.5^\circ$ . Similar results are obtained with nitrosodimethylaniline, a substance melting at  $212^\circ$  being formed which closely resembles the *p*-nitrobenzaldehyde-*p*-dimethylaminoanil, which melts at  $217^\circ$ . Some impurity must therefore be present which cannot at present be removed.

A. H.

Action of Paraldehyde on *o*-Nitrosobenzoic Acid. By GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1902, 35, 1080—1081). —*o*-Nitrosobenzoic acid in paraldehyde solution is converted slowly by bright sunlight, more rapidly by heating, into a crystalline substance,  $C_9H_7O_3N$ , melting at  $121^\circ$ , and isomeric, not identical, with *o*-nitrocinnamaldehyde.

W. A. D.

A cycloKetotriose and its Conversion into Methyl-*o*-diketocyclohexane. By CARL D. HARRIES (*Ber.*, 1902, 35, 1176—1178).

—Dihydroxymethylcyclohexanone,  $OH \cdot CMe \begin{matrix} \text{CH(OH) \cdot CO} \\ \text{CH}_2 \text{---CH}_2 \end{matrix} CH_2$ ,

obtained when methylcyclohexenone or  $\Delta^{13}$ -dihydrotoluene (see this vol., i, 361) is oxidised in aqueous acetone solution with permanganate, crystallises in cubes, melts at  $52^\circ$ , boils at  $108$ — $110^\circ$  under 12 mm. pressure, gives a green coloration with ferric chloride, and reduces silver nitrate and Fehling's solution in the cold; the phenylhydrazone crystallises in small, yellowish needles, which sinter at  $140^\circ$  and melt at  $143^\circ$ , and the semicarbazone crystallises from water and melts and decomposes at  $221$ — $222^\circ$ . When warmed with 2 mols. of phenylhydrazine, the hexanone yields a compound which melts at  $128^\circ$  and appears to be a normal osazone from which a mol. of water has been eliminated. When boiled with 5 per cent. sulphuric acid, the hexanone yields methyl-*o*-diketocyclohexane,  $CHMe \begin{matrix} \text{CO---CO} \\ \text{CH}_2 \text{---CH}_2 \end{matrix} CH_2$ , which crystallises from light petroleum, melts at  $64$ — $65^\circ$ , and is soluble in boiling sodium hydroxide; the diphenylhydrazone crystallises in yellow needles and melts at  $152^\circ$ , whilst the monophenylhydrazone (?) melts at  $103^\circ$ ; the semicarbazones melt respectively at  $182^\circ$  and  $244^\circ$ .

R. H. P.

**Condensation of Carbon Tetrachloride with Halogen Derivatives of Benzene by means of the Friedel and Crafts Reaction.** By JAMES F. NORRIS and ERIK H. GREEN (*Amer. Chem. J.*, 1901, 26, 492—499).—4 : 4'-*Dichlorobenzophenone chloride* was obtained by the action of chlorobenzene on carbon tetrachloride in carbon disulphide solution in presence of aluminium chloride. It is a pale green, viscid liquid, distils at 217—219° (corr.) under 38 mm. pressure, and is soluble in carbon disulphide or ether, slightly so in alcohol, and insoluble in water. It dissolves in concentrated sulphuric acid with evolution of hydrogen chloride, and on dilution the ketone is precipitated.

4 : 4'-*Dichlorobenzophenone* is readily obtained from the above by boiling with dilute alcohol; it crystallises in plates, melts at 144·5°, and is easily soluble in carbon disulphide, chloroform, ether, glacial acetic acid, or acetone.

4 : 4'-*Dibromobenzophenone*, prepared in the same way from bromobenzene, melts at 171—172°, and is soluble in carbon disulphide, chloroform, benzene, or hot alcohol, but only slightly so in ether.

2 : 5 : 2' : 5'-*Tetrachlorobenzophenone chloride*, obtained from *p*-dichlorobenzene and carbon tetrachloride in carbon disulphide solution with aluminium chloride, melts at 173—174°, is soluble in chloroform, benzene, or acetone, less so in ether, and only slightly in hot alcohol or concentrated sulphuric acid. It is converted into the corresponding ketone, 2 : 5 : 2' : 5'-*tetrachlorobenzophenone*, by boiling with dilute alcohol; this separates from alcohol in colourless crystals which melt at 128°, and is readily soluble in hot alcohol, carbon disulphide, benzene, acetone, ethyl acetate, or chloroform.

J. McC.

**Condensation of Aromatic Ketones.** By R. SORGE (*Ber.*, 1902, 35, 1065—1074).—The *semicarbazone* of cinnamylideneacetophenone,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CPh}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , crystallises from ether. The corresponding *phenylhydrazone* crystallises from alcohol in brownish-yellow prisms and melts at 125—126°. By reduction with tin and alcoholic hydrogen chloride, the ketone is converted into *α*-*diphenyl-α*-pentanol,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{OH}$ , which crystallises from alcohol and melts with partial decomposition at 80—81°.

*o*-*Nitrobenzylideneacetophenone*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COPh}$ , crystallises from alcohol in minute, felted needles and melts at 124°; the *semicarbazone* crystallises from alcohol in minute, hair-like, felted, golden-yellow needles and melts at 177·5°; the *dibromide*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{COPh}$ , crystallises from chloroform in short, yellowish-white, four-sided prisms, melts at 167—168°, and becomes brown and decomposes in the air.

*m*-*Nitrobenzylideneacetophenone* crystallises from benzene in microscopic, yellow needles and melts at 145—146°; the *dibromide* crystallises from chloroform in colourless rhombohedra, does not dissolve in ordinary solvents, and melts at 187°.

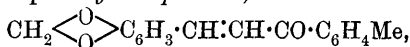
*p*-*Nitrobenzylideneacetophenone* crystallises from benzene in microscopic tablets and melts at 164°; the *semicarbazone* forms minute, yellow, glistening scales and melts at 178—179°; the *dibromide* crystal-

lises from chloroform in small, slender, white prisms, melts at  $148^{\circ}$ , and slowly decomposes in air.

The *hydrazide* of *p*-tolyl methyl ketone (Claus and Wollner, Abstr., 1885, 1136),  $C_6H_4Me \cdot CMe \cdot N \cdot NH_2$ , separates from alcohol in yellow, rhombic crystals and melts at  $131-132^{\circ}$ ; the *semicarbazone* forms small, glistening, white crystals and melts at  $204-205^{\circ}$ .

*Benzylidene-p-methylacetophenone*,  $CHPh \cdot CH \cdot CO \cdot C_6H_4Me$ , crystallises from alcohol in yellow tablets and melts at  $59-60^{\circ}$ .

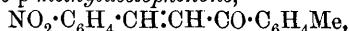
*Piperonylidene-p-methylacetophenone*,



separates from alcohol in glistening, golden crystals and melts at  $130^{\circ}$ ; the *phenylhydrazone* crystallises from alcohol in yellow, prismatic tablets and melts at  $135^{\circ}$ .

The *ketone*,  $CH_2 \begin{array}{c} \diagup O \diagdown \\ \diagdown O \diagup \end{array} C_6H_3 \cdot CH \cdot CH \cdot CH \cdot CH \cdot CO \cdot C_6H_4Me$ , crystallises from alcohol in yellowish-brown nodules and melts at  $118-119^{\circ}$ .

*o-Nitrobenzylidene-p-methylacetophenone*,



crystallises from alcohol in minute, glistening, rectangular tablets and melts at  $106-107^{\circ}$ ; the *semicarbazone*,  $C_{17}H_{16}O_3N_4$ , crystallises from alcohol in small, yellow, glistening, prismatic needles and melts at  $111^{\circ}$ .

*m-Nitrobenzylidene-p-methylacetophenone* crystallises from alcohol or carbon disulphide in hair-like, felted, yellow needles and melts at  $137^{\circ}$ ; the *semicarbazone* crystallises from alcohol in hair-like needles and melts at  $140^{\circ}$ .

*p-Nitrobenzylidene-p-methylacetophenone* crystallises from alcohol in yellow, hair-like needles and melts at  $161^{\circ}$ , the *semicarbazone* melts at  $200^{\circ}$ .

*n-Propylphenylketoxime*,  $CPhPr^o \cdot NOH$ , crystallises from ether in colourless, hygroscopic needles and melts at  $49-50^{\circ}$ . The *phenylhydrazone*,  $C_3H_7 \cdot CPh \cdot N \cdot NHPh$ , is an oil; its *hydrochloride* crystallises from alcohol and melts at  $199-201^{\circ}$ . The *semicarbazone*,  $C_3H_7 \cdot CPh \cdot N \cdot NH \cdot CO \cdot NH_2$ , crystallises from alcohol in prisms and melts at  $188^{\circ}$ .

T. M. L.

**Dibenzylideneacetone and Triphenylmethane. A Contribution to the Theory of Dyes.** By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1902, 35, 1189—1201. Compare Abstr., 1902, i, 112).—The salts of dibenzylideneacetone, which is itself colourless, are deeply coloured, a phenomenon termed by the authors *halochromism*. The production of coloured salts in this case cannot be ascribed to the acetone group itself, since the salts of dimethylpyrone are colourless, but is due to this group combined with two benzene rings. That the salts are true salts and have not a quinonoid constitution is proved by the fact that precisely similar phenomena are shown by dianisylideneacetone, in which case the salts are formed without any elimination of methyl alcohol, which would occur if they had a quinonoid constitution.

*Anisylideneacetone* is prepared from anisaldehyde and acetone and crystallises in long, colourless plates melting at  $72-74^{\circ}$ . It is slightly halochromic, forming a yellow solution in hydrochloric acid.

*Dianisylideneacetone* crystallises in long, yellow plates melting at 129—130°; it is more basic than dibenzylideneacetone, and forms more deeply coloured salts. The *sulphate*,  $2C_{19}H_{18}O_3 \cdot 3H_2SO_4$ , crystallises in opaque, violet needles, and when treated with water yields unaltered dianisylideneacetone. The *hydrochloride* crystallises in bluish-red cubes, the *hydriodide* forms black, hair-like needles, and the *picrate* crystallises in yellowish-red, rhombic plates. It follows from the foregoing that the presence of the benzene ring in certain compounds is sufficient to render them chromophoric. Benzene itself is not halochromic, since it, like naphthalene and some other hydrocarbons, is not coloured by sulphuric acid. On the other hand, triphenylmethane forms a yellow solution in sulphuric acid, and is therefore halochromic.

The yellow colour is not due to the formation of triphenylcarbinol by oxidation, since the colour is discharged by acetic acid, whilst that of a solution of the carbinol in sulphuric acid is not affected by this reagent. It appears probable that the yellow compounds of triphenylmethyl chloride, with aluminium chloride and other negative chlorides, owe their yellow colour, not to a quinonoid constitution, but to the fact that the presence of the negative chloride converts the ester-like triphenylmethyl chloride into a true salt, in which the halochromism of the group becomes evident. This view is rendered probable by the behaviour of the more strongly basic *trianisylmethane*,  $CH(C_6H_4 \cdot OMe)_3$ , which is prepared from anisole and anisaldehyde and crystallises in long needles melting at 45—47°. It dissolves in sulphuric acid, forming a red solution from which it is precipitated unchanged by water. The analogous amino-compound, hexamethyltriaminotriphenylmethane, on the other hand, is not halochromic. Since triphenyl-leucaniline itself is also not halochromic, it appears probable that oxonium salts may be distinguished from ammonium salts by the possession of this property, but this cannot yet be considered as definitely proved. *Trianisylcarbinol*,  $C(C_6H_4 \cdot OMe)_3 \cdot OH$ , forms large, colourless crystals melting at 83·5—84°. It behaves towards acids like triphenylcarbinol, but forms both carbonium and oxonium salts. The *chloride* is colourless, but yields coloured compounds with negative chlorides. The *nitrate* and *sulphate* are coloured and are probably true salts.

The chloride unites with hydrogen chloride to form a red oxonium salt. On decomposition, these salts yield unaltered trianisylcarbinol, so that no quinonoid change has occurred. The elimination of the methyl group, in fact, only takes place very slowly.

*Dianisylphenylmethane* is prepared from anisole and benzaldehyde and crystallises in needles melting at 100—100·5°. A. H.

[1:8-Dihydroxynaphthaketones.] MARTIN LANGE (D.R.-P. 126199).—1:8-Dihydroxy-2-acetonaphthone,  $C_{10}H_5(OH)_2 \cdot COMe$ , prepared by condensing 1:8-dihydroxynaphthalene with glacial acetic acid in the presence of zinc chloride, melts at 100—101° and forms a *diacetyl* derivative melting at 168—169°.

1:8-Dihydroxy-2-propionaphthone,  $C_{10}H_5(OH)_2 \cdot COEt$ , and 1:8-dihydroxy-2-isobutyronaphthone,  $C_{10}H_5(OH)_2 \cdot CO \cdot CHMe_2$ , melt at 101—102° and 88° respectively; the *diacetyl* derivative of the latter melts at 105—106°.

1:8-Dihydroxy-2-isovaleronaphthone,  $C_{10}H_5(OH)_2 \cdot CO \cdot CH_2Pr^{\beta}$ , melts at 71—72°, and its diacetyl derivative at 110—111°.

1:8-Dihydroxy-2-benzonaphthone,  $C_{10}H_5(OH)_2 \cdot COPh$ , produced by condensing 1:8-dihydroxynaphthalene with benzoic acid, benzoyl chloride, or benzoic anhydride, melts at 121—122°; its *diacetyl* compound melts at 115—116°. These ketones crystallise from alcohol in yellow or orange-coloured needles, they condense with aromatic amines and diazonium salts, produce orange-coloured lakes with alumina, and yield an intense green precipitate with ferric chloride. G. T. M.

1:4-Nitroacetylaminanthraquinone and 1:4-Nitroaminanthraquinone. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 125391. Compare *Ber.*, 1882, 15, 1790).—4-Nitro-1-acetylaminanthraquinone, produced by treating a solution of acetyl-1-aminanthraquinone in concentrated sulphuric acid with 20 per cent. nitric acid at 15°, crystallises from epichlorohydrin, pyridine, or glacial acetic acid in golden-yellow needles and melts at 256—258°. 4-Nitro-1-aminanthraquinone, prepared either by performing the nitration at 90—100° or by hydrolysing the acetyl compound, crystallises from epichlorohydrin in yellowish-red needles and melts at 290—295°. G. T. M.

Polychlorodiaminoanthraquinones. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 125094).—The perchlorinated diaminoanthraquinone, consisting chiefly of *octochloro-1:5-diaminoanthraquinone*, obtained by treating 1:5-diaminoanthraquinone dissolved in glacial acetic acid with chlorine gas, is a yellow powder readily soluble in the ordinary organic solvents, but not in cold concentrated sulphuric acid; it sinters at 90° and melts at 100°. When treated with alkalis or reducing agents, the substance yields products, such as the penta- or tetra-chloro-derivatives, containing less chlorine. G. T. M.

Arylamino-nitroanthraquinones. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 126542).—The 1:5-, 1:7-, and 1:8-dinitroanthraquinones, when heated with a primary aromatic amine, exchange one of their nitro-groups for the arylamino-residue,  $R \cdot NH$ , yielding arylaminonitroanthraquinones. Diarylaminoanthraquinones, however, are formed when the reaction is prolonged.

8-Anilino-1-nitroanthraquinone crystallises in bluish-violet needles.

7-p-Toluidino-1-nitroanthraquinone, produced from 1:7-dinitroanthraquinone and *p*-toluidine, crystallises from acetone in violet-black needles.

5- $\alpha$ -Naphthylamino-1-nitroanthraquinone crystallises from glacial acetic acid in brownish-violet needles.

These condensations are effected either by heating the reagents at 130—160°, or by mixing them together in boiling pyridine.

G. T. M.

Bromo-derivatives from Aminohydroxyanthraquinones. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 126015).—When treated with bromine, the amino- or hydroxy-anthraquinones yield bromo-derivatives of the original compounds. The aminohydroxyanthra-



quinones, however, exchange their amidogen radicles for hydroxyl under these conditions, and are simultaneously brominated; thus,  $\beta$ -aminoalizarin yields bromoanthragallol (m. p. 217°), and  $\beta$ -amino-anthrapurpurin and  $\beta$ -amino-flavopurpurin similarly furnish bromo-hydroxyanthragallols.

G. T. M.

**Anthragallolsulphonic Acid.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 125575).—*Sodium anthragallolsulphonate*, produced by boiling the bromoanthragallol from  $\beta$ -aminoalizarin with a concentrated solution of sodium hydrogen sulphite, crystallises on cooling in yellowish-red needles. The *acid*, prepared by using sulphurous acid instead of the sulphite, yields anthragallol when heated with sulphuric acid.

G. T. M.

**Conversion of Nitroanthraquinone Derivatives into the corresponding Hydroxy-compounds.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 125579).—Many nitro-compounds of the anthraquinone series, when heated with concentrated sulphuric acid containing boric acid, become converted into the corresponding hydroxy-derivatives, the nitro-group being eliminated as nitrous acid. The change is due to a specific action of the boric acid, for in the absence of this reagent the hydroxyl compound is not produced. At 80—90°, 4 : 8-dinitroanthrarufin-2 : 6-disulphonic acid is converted into 8-nitro-1 : 4 : 5-trihydroxy-2 : 6-anthraquinonedisulphonic acid, and at 120—150° the remaining nitro-group is removed, and 1 : 4 : 5 : 8-tetrahydroxy-anthraquinone-2 : 6-disulphonic acid is obtained.

In a similar manner, 4 : 8-dinitroanthrarufin, which is not affected by sulphuric acid alone at 150°, is converted by a mixture of this reagent and boric acid first into 8-nitro-1 : 4 : 5-trihydroxyanthraquinone, and then into 1 : 4 : 5 : 8-tetrahydroxyanthraquinone.

The patent contains several other examples of this reaction and a table showing the properties of the products.

G. T. M.

**Variation in the Rotatory Power of the Esters of *l*-Borneol.** By JULES MINGUIN and E. GRÉGOIRE DE BOLLEMONT (*Compt. rend.*, 1902, 134, 608—610).—The authors have determined the rotatory power of a number of esters prepared from N'ghai borneol, and the results are contained in the following table. In the absence of accurate knowledge of the constitution of borneol, it is not possible to discuss the results on the basis of Guye's theory, but it is noteworthy that in the esters of the acetic series, the rotatory power is approximately inversely proportional to the molecular weight, and this holds good also for the halogen derivatives of the acids of the same series :

	Mol. wt.	Boiling point.	[ $\alpha$ ] <sub>D</sub> .
N'ghai borneol .....	154	—	— 38·09°
Bornyl formate .....	182	215°	— 49
„ acetate.....	196	223	— 45·5
„ propionate .....	210	235	— 42·8
„ butyrate .....	224	246—247	— 40·01
„ isobutyrate .....	224	242—244	— 40·01

c c z

	Mol. wt.	Boiling point.	$[\alpha]_D$ .
Bornyl chloroacetate .....	230.5	263°	- 39.6°
„ valerate .....	238	—	- 37.4
„ dichloroacetate .....	265	269—270	- 29.6
„ bromoacetate .....	275	265	- 30.5
„ $\alpha$ -bromopropionate ...	289	271—273	- 26.8
„ trichloroacetate .....	299.5	276—277	- 25.7
„ $\alpha$ -bromoisobutyrate ..	303	150 (19 mm.)	- 27.5
„ $\alpha$ -bromobutyrate .....	303	168 (19 mm.)	- 26.4
„ trichlorobutyrate ...	327.5	195 (19 mm.)	- 20.5
„ laurate .....	336	250 (40 mm.)	- 27.7
„ $\alpha\alpha$ -dibromopropionate	368	190 (20 mm.)	- 20.2
„ tribromoacetate .....	433	m. p. 61	- 19.03

C. H. B.

**Basic Properties of Quadrivalent Oxygen.** By OTTO SACKUR (*Ber.*, 1902, 35, 1242—1252).—Measurements of the conductivity of solutions of cineol in hydrochloric acid show that cineol hydrochloride is completely dissociated hydrolytically into acid and base. The basicity of cineol is, however, proved by the fact that its solubility in dilute acids is greater than in pure water, the solubility increasing with the concentration of the acid; a similar method has already been applied to ethyl ether (compare Jüttner, *Abstr.*, 1901, ii, 595). Another proof is given by the fact that the diminution of the solubility in water of cineol, caused by the presence of a base such as potassium or sodium hydroxide, is much greater than that due to a neutral salt such as sodium chloride.

Measurements are given showing that the molecular conductivity of dry hydrogen chloride in ether, amyl alcohol, or cinnamaldehyde, diminishes with increasing dilution, a fact indicating the basic nature of these substances; with aniline and *o*-toluidine, similar observations were made, but with nitrobenzene, benzaldehyde, and acetone, which must be considered non-basic in character, an increase in conductivity was observed.

A discussion of the nature of the salts of dimethylpyrone and of the basicity of cinnamaldehyde closes the paper. W. A. D.

**Oxidation of Menthone, Pulegone, and  $\beta$ -Methylhexanone.** By NICOLAI A. SPERANSKY (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 10—17).—Various investigators have ascribed different melting points to  $\beta$ -methyladipic acid obtained by the oxidation of menthone, pulegone, and  $\beta$ -methylhexanone, reactions which the author has now examined.

Whether oxidised by potassium permanganate or by concentrated or dilute nitric acid, methylhexanone yields only  $\beta$ -methyladipic acid melting at 67°. This was shown by the action of benzaldehyde on the acid obtained, which yielded only dibenzylidene- $\beta$ -methylpentanone and no monobenzylidene- $\alpha$ -methylpentanone, as should be the case if any  $\alpha$ -methyladipic acid were present.

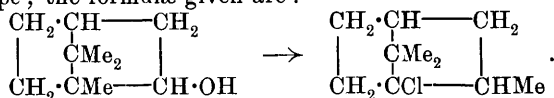
The  $\beta$ -methyladipic acid obtained by the oxidation of pulegone with permanganate is found to contain a certain quantity of its anhydride, which with aniline forms an *anilino-acid*,  $C_{13}H_{11}O_3N$ , separating from ether in crystals melting at 120°. The  $\beta$ -methyladipic acid free from

anhydride melts at  $91^{\circ}$  and has  $[\alpha]_D + 8^{\circ}38'$ . The acid obtained from menthone melts at  $84^{\circ}$ , has  $[\alpha]_D + 9^{\circ}48'$  and with benzaldehyde gives dibenzylidene- $\beta$ -methylpentanone; it is probable that there is anhydride present in this acid but this has not been confirmed.

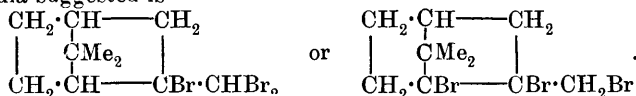
*Benzylidene- $\alpha$ -methylpentanone*,  $\begin{array}{c} \text{CH}_2\text{---CHMe} \\ \text{CH}_2\cdot\text{C}(\text{CHPh}) \end{array} > \text{CO}$ , obtained by the condensation of benzaldehyde with  $\alpha$ -methylpentanone, separates from a mixture of ether and light petroleum in bundles of long, silky, white crystals melting at  $123\text{--}124^{\circ}$ ; it is readily soluble in ether or ethyl acetate and is coloured brown by strong sulphuric acid.

T. H. P.

**Camphene and Camphor.** By FRIEDRICH W. SEMMLER (*Ber.*, 1902, 35, 1016—1022. Compare *Abstr.*, 1901, i, 90).—It is suggested that the formation of *isobornyl* chloride by the action of phosphorus pentachloride on borneol is due to an isomeric change of the Beckmann type; the formulæ given are:



*Bromocamphene dibromide*,  $\text{C}_{10}\text{H}_{15}\text{Br}_2$ , prepared by the action of bromine on bromocamphene, crystallises from alcohol, melts at  $77\text{--}78^{\circ}$ , and is inactive. *Chlorocamphene dichloride*,  $\text{C}_{10}\text{H}_{15}\text{Cl}_2$ , boils at  $130\text{--}135^{\circ}$  under 10 mm. pressure and melts at  $135^{\circ}$ . The formula suggested is



The formula of camphorophorone,  $\begin{array}{c} \text{CH}_2\cdot\text{C}(\text{CMe}_2) \\ \text{CH}_2\text{---CHMe} \end{array} > \text{CO}$ , previously suggested (*Ber.*, 1892, 25, 3520) is confirmed by experiments on the reduction and subsequent oxidation of the compound, but details are not yet given.

T. M. L.

**Camphidone and Camphidine.** C. F. BOEHRINGER & SÖHNE (D.R.-P. 126196).—*Camphidone*,  $\text{C}_{10}\text{H}_{17}\text{ON}$ , produced by electrolysis in the cathode cell a solution of camphorimide in 65 per cent. sulphuric acid, is isolated by partly neutralising the product with calcium carbonate and extracting the solution with chloroform; it melts at  $220^{\circ}$ , boils at  $308^{\circ}$ , and is soluble in all the ordinary solvents with the exception of cold water; its picrate crystallises in yellow needles. *Camphidine*,  $\text{C}_{10}\text{H}_{19}\text{N}$ , is obtained from the mother liquors in the preceding reduction by adding excess of alkali hydroxide and distilling in steam; it is a soft, white, crystalline substance, melting at  $188^{\circ}$  and boiling at  $209^{\circ}$ .

G. T. M.

*cyclo*Citral. HAARMANN & REIMER (D.R.-P. 123747).—Citral, when condensed with aniline and ethylamine, yields citralideneaniline and citralidene-ethylamine respectively; these substances are oils. When

slowly added to cold concentrated sulphuric acid, they give rise to products which, when diluted with water and distilled in steam, furnish *cyclocitral*. The crude cyclic aldehyde boils at 85—100° under 16 mm. pressure, and when purified by means of its semicarbazone yields *β-cyclocitral*. Phosphoric acid may be employed to bring about the transformation, and in this case the mixture is gently warmed.

G. T. M.

**Synthesis in the Terpene Series by Means of Haloid Compounds of Aluminium.** By MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 31—33).—*Phenyldihydropinenene*,  $C_{10}H_{17}Ph$ , prepared by the interaction of carefully dried pinene hydrochloride and benzene in presence of aluminium chloride, boils at 286—291° under 745 mm. pressure and has the normal molecular weight in freezing benzene; it has the sp. gr. 0.9594 at 20°/0° and  $n_D$  1.52691 at 20°. The hydrocarbon exhibits the usual characters of saturated compounds and reacts vigorously with dilute nitric acid. T. H. P.

**Proximate Analysis of the Essence of *Mentha Pulegium*.** By LÉON TÉTRY (*Bull. Soc. Chim.*, 1902, [iii], 27, 186—193. Compare Abstr., 1891, 936).—From essence of Polei, by fractional distillation under 20 mm. pressure, the author obtained three fractions boiling below 105°, between 105° and 110°, and between 110° and 112° respectively. The last fraction consists chiefly of pulegone, but also contains menthol (about 10 per cent.) and possibly also  $\alpha$ - or  $\beta$ -isopulegone. The lower boiling fractions contain menthone and probably some terpenes, but the latter could not be sufficiently characterised.

A. F.

**Essence of Sweet Orange Blossom or Neroli Portugal.** By EUGÈNE THEULIER (*Bull. Soc. Chim.*, 1902, [iii], 27, 278—280).—When obtained by the simple distillation of the blossoms, the essence forms a dark yellow liquid, the odour of which does not at all resemble that of the ordinary oil of neroli. The author has discovered the presence in it of *d*-camphene, *d*-limonene, and of *d*-linalool, but owing to the loss of a considerable portion, the examination of the oil is incomplete. The presence of methyl anthranilate could not be detected. On cooling the essence, crystalline lamellæ are obtained, which melt at 55° and readily volatilise without decomposition.

A. F.

**Behaviour of Crude Caoutchouc towards Concentrated Nitric Acid.** By RUDOLF DITTMAR (*Ber.*, 1902, 35, 1401—1402. Compare Harries, Abstr., 1901, i, 733).—Crude caoutchouc is vigorously attacked by concentrated nitric acid and yields a yellowish-red substance, which is purified by repeated precipitation of its solution in ethyl acetate by ether; it begins to decompose at 142—143°, is readily soluble in alkalis, forming a blood-red solution. Analysis and a molecular weight determination show that it has the formula  $C_{10}H_{12}O_6N_2$ , and on titration with sodium hydroxide and phenolphthalein it behaves as a monobasic acid.

K. J. P. O.

**Saponarin, a New Glucoside from Saponaria.** By GEORGE BARGER (*Ber.*, 1902, 35, 1296—1298).—Saponarin dissolves in about 1000 parts of hot water and crystallises on cooling in minute, birefringent needles. It dissolves in alkalis with an intense yellow colour, and gives a blue colour with a solution of iodine in potassium iodide; the blue colour is destroyed by large excess of water, by alcohol, ether, or chloroform and by warming. It gives a brownish-red colour with ferric chloride, a yellow precipitate with lead acetate, and a white precipitate with silver nitrate. It contains  $C = 50.66$ ,  $H = 6.30$ , loses water in a vacuum or at  $100^\circ$ , and when dry is very hygroscopic. It is hydrolysed by mineral acids with formation of dextrose, and a substance which still reacts like saponarin, but gives no blue coloration with iodine; *p*-hydroxybenzoic acid was isolated from the product, together with an aromatic alcohol, probably quinol. Saponarin resembles Molisch and Goldschmiedt's scutellarin (this vol., i, 48) and is perhaps the glucoside of a flavone derivative.

T. M. L.

**Artemisin.** By PAUL HORST (*Chem. Zeit.*, 1902, 26, 203).—Artemisin ( $C_{15}H_{18}O_4$ ), on oxidation with potassium permanganate, gives *artemic acid*,  $C_{14}H_{16}O_4$ , which forms prismatic, colourless crystals, melts at  $179-181^\circ$ , and is readily soluble in alcohol, but only sparingly so in water or ether.

J. McC.

**Theory of Dyeing.** By EDMUND KNECHT (*Ber.*, 1902, 35, 1022—1024).—Silk dyed with "night-blue" can be completely decolorised by extraction with alcohol; when the alcoholic extract is poured into baryta-water, the colour-base is precipitated, but the solution, when filtered and precipitated with carbon dioxide, gives a coloured precipitate when treated again with "night-blue" or with magenta. This behaviour is explained by supposing that the base combines with a compound similar to sericic acid, forming a lake insoluble in water but soluble in alcohol, which therefore extracts from the fibre the acid constituent as well as the basic dye.

T. M. L.

**Chlorophyll.** By LEO MARCHLEWSKI (*J. pr. Chem.*, 1902, [ii], 65, 161—167).—A mixture of the imide and anhydride of hæmatic acid is obtained when phylloporphyrin is oxidised with potassium chromate in acetic acid solution (see Abstr., 1901, i, 298). The product obtained by the reduction of phyllocyanin with zinc dust is identical with the hæmopyrrole previously obtained by the author and Nencki (Abstr., 1901, i, 554).

Phylloporphyrin is a fairly strong base, the salts of which give absorption spectra quite different to that of the base itself, and comparison of the spectra given by very dilute aqueous solutions of the base and of the salts leads to the conclusion that practically no hydrolytic dissociation has occurred with the latter. As, however, all the salts in very dilute solutions of equal molecular strength give identical spectra, it must be assumed that electrolytic dissociation has taken place, and that the spectrum is that of the coloured positive ion  $C_{16}H_{19}ON_2^+$ .

R. H. P.

**Bile-pigments.** By WILLIAM KÜSTER (*Ber.*, 1902, **35**, 1268—1278).—The pigments isolated from gall-stones are not necessarily present as such, but may have been formed during the process of extraction. The fraction soluble in chloroform contains at least two substances; bilirubin is soluble in 600 parts of chloroform, but is accompanied by a brownish-green pigment which contains less nitrogen, dissolves in 30 parts of chloroform, dissolves readily in dimethylaniline, but does not separate well on cooling and is soluble in alkalis to a deep red liquid. To free the bilirubin from this substance, it must be repeatedly extracted with chloroform; the product is then separated from bilirubin by extraction with alcohol, and when dissolved in hot dimethylaniline separates on cooling in beautiful crystals having the composition  $C_{16}H_{18}N_2O_3$ . Bilirubin is appreciably soluble in ethyl benzoate and dissolves in 30 parts of *iso*amyl benzoate, half of the substance separating on cooling in indistinct crystals.

A summary is given of the results which have been obtained in establishing a relationship between the bile and blood pigments and especially between the isomeric bilirubin and hæmatoporphyrin. T. M. L.

**$\delta$ -Nitropyromucic Acid.** By HENRY B. HILL and GEORGE R. WHITE (*Amer. Chem. J.*, 1902, **27**, 193—205).—By the action of nitric acid on  $\delta$ -sulphopyromucic acid,  $\delta$ -nitropyromucic acid, dinitrofurfuran, and nitrofurfuransulphonic acid are produced. If nitric acid is allowed to act on a solution of pyromucic acid in fuming sulphuric acid, nitropyromucic acid and dinitrofurfuran are obtained, but no nitrofurfuransulphonic acid can be isolated.

*Potassium nitrofurfuransulphonate* crystallises in rectangular prisms; when treated with concentrated nitric acid, it yields dinitrofurfuran. If the salt is heated with hydrobromic acid at  $100^\circ$  in a sealed tube, hydroxylamine, sulphuric acid, and an acid (probably bromosuccinic) melting at  $160$ — $161^\circ$  are produced.

*aa*-Dinitrofurfuran, first obtained by Hill and Palmer (*Abstr.*, 1889, **37**), crystallises from alcohol in pale yellow, slender prisms, melts at  $101^\circ$ , and sublimes at a lower temperature; it is soluble in ether, benzene, hot alcohol, or hot chloroform and is volatile with steam. It is readily attacked by barium hydroxide with formation of barium nitrite and maleate.

*Aniline  $\delta$ -nitropyromucate* crystallises in colourless leaflets. If aniline hydrochloride is added to nitropyromucic acid dissolved in solution of sodium acetate, carbon dioxide is evolved and a red precipitate is produced which consists of a mixture of two substances, one of which is yellow and the other crimson. The yellow substance,  $C_{16}H_{13}ON_3$ , forms stellate groups of rectangular crystals, melts at  $232^\circ$ , and is soluble in glacial acetic acid; on reduction with zinc dust and acetic acid, it yields succinil, aniline, and ammonia. The crimson substance,  $C_{17}H_{13}O_3N_3$ , crystallises from hot glacial acetic acid in flat needles, melts and decomposes at  $218^\circ$ , and is readily soluble in chloroform or benzene.

Corresponding compounds were obtained from *p*-toluidine. The yellow substance,  $C_{18}H_{17}ON_3$ , crystallises from glacial acetic acid in groups of prisms and melts at  $250^\circ$ ; on reduction, it yields ammonia, *p*-toluidine, and a substance melting at  $153$ — $154^\circ$  which is probably

a tolylsuccinimide. The crimson *compound*,  $C_{19}H_{17}O_3N_3$ , crystallises from glacial acetic acid in needles and decomposes on heating.

E. G.

**Cyclic Compounds containing Sulphur.** By WILHELM AUTENRIETH and R. HENNINGS (*Ber.*, 1902, 35, 1388—1400. Compare Abstr., 1901, i, 560).—To *o*-xylylene mercaptan and formaldehyde in solution in mol. proportions are added a few drops of concentrated hydrochloric acid; a reaction takes place, with the formation of cyclo-*o*-xylylene-1 : 3-dithio-2-methylene,  $C_6H_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{S} \\ \text{CH}_2 \cdot \text{S} \end{smallmatrix} > CH_2$ , which crystallises in prisms melting at  $152-153^\circ$ ; on oxidation with acid potassium permanganate, the corresponding *disulphone* is obtained crystallising in prisms melting above  $300^\circ$ , and is soluble in alkali hydroxides and carbonates. When boiled with bromine water, a *dibromide*,  $C_6H_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{SO}_2 \\ \text{CH}_2 \cdot \text{SO}_2 \end{smallmatrix} > CBr_2$ , is produced; it forms prisms melting and decomposing at  $250^\circ$ .

cyclo-*o*-Xylylene-1 : 3-dithio-2-methylmethylene,  $C_6H_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{S} \\ \text{CH}_2 \cdot \text{S} \end{smallmatrix} > CHMe$ , prepared from *o*-xylylene mercaptan and acetaldehyde, crystallises in needles melting at  $110^\circ$  and yields, on oxidation, a *disulphone* which forms lustrous leaflets melting and decomposing above  $300^\circ$ ; with bromine water, the disulphone gives a *monobromide* which melts and decomposes at  $250^\circ$ . It is found that cyclo-2-methyltetramethylene-1 : 3-disulphone, when treated with bromine water, yields a *bromide*,  $CH_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{SO}_2 \\ \text{CH}_2 \cdot \text{SO}_2 \end{smallmatrix} > CMeBr$ , which crystallises in long needles melting at  $208-210^\circ$ . cyclo-*o*-Xylylene-1 : 3-dithio-2-phenyl-2-methylmethylene  $C_6H_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{S} \\ \text{CH}_2 \cdot \text{S} \end{smallmatrix} > CMePh$ , prepared from *o*-xylylene mercaptan and acetophenone, melts at  $126^\circ$  and is oxidised to a *disulphone* which crystallises in leaflets melting at  $202^\circ$ .

*o*-Xylylenedibenzylthioether,  $C_6H_4(CH_2 \cdot SO_2 \cdot C_7H_7)_2$ , is obtained from *o*-xylylenedibenzylthio-ether, which is prepared by mixing in alcoholic solution *o*-xylylene mercaptan, benzyl chloride, and sodium ethoxide; the disulphone crystallises in needles melting at  $195^\circ$ .

*m*-Benzenedisulphoneanilide,  $C_6H_4(SO_2 \cdot NHPh)_2$ , prepared from *m*-benzenedisulphonic chloride and aniline, crystallises in needles melting at  $143^\circ$  and soluble in alkali hydroxides and carbonates; *dibenzyl-m-benzenedisulphonanilide*,  $C_6H_4(SO_2 \cdot NPh \cdot C_7H_7)_2$ , obtained by boiling a solution of the anilide and sodium ethoxide in alcohol with excess of benzyl chloride, crystallises in needles melting at  $170^\circ$ ; the *diacetyl* derivative, prepared from the anilide and acetic anhydride, forms prisms melting at  $171^\circ$ . Neither by the action of iodine on the mercury or silver salts of the sulphoneanilide, nor by the action of methylene iodide or ethylene bromide on the sodium salt, could the formation of a ring be induced.

*m*-Phenylene-di-iodomethylthioether,  $C_6H_4(SO_2 \cdot CH_2I)_2$ , is obtained by heating potassium *m*-benzenedisulphinate and methylene iodide

under pressure at  $150^{\circ}$  and crystallises in leaflets melting at  $263\text{--}265^{\circ}$ .

On acidifying with dilute sulphuric acid, a solution containing equivalent quantities of potassium *m*-benzenedisulphinate and sodium nitrite, *m*-benzenedisulphonohydroxamic acid (*m*-benzenedisulphonohydroxylamine),  $\text{C}_6\text{H}_4\cdot(\text{SO}_2)_2\cdot\text{N}\cdot\text{OH}$ , is formed; it crystallises in white needles decomposing at  $215^{\circ}$ , is soluble in alkali hydroxides and carbonates, and is easily hydrolysed by boiling water to the disulphinic acid and nitrous acid.

*m*-Phenylenedibenzylidisulphone,  $\text{C}_6\text{H}_4(\text{SO}_2\cdot\text{C}_6\text{H}_5)_2$ , prepared from potassium *m*-benzenedisulphinate and benzyl chloride in the presence of alcohol, crystallises in lustrous leaflets melting at  $240^{\circ}$ .

It is shown that the disulphones herein described are not hydrolysed by boiling alkali hydroxides; only  $\beta$ -disulphones, in which the two sulphone groups are attached to neighbouring carbon atoms, can thus be hydrolysed. K. J. P. O.

**Extraction of Alkaloids from Alkaline Liquids.** By EDMUND SPRINGER (*Chem. Centr.*, 1902, i, 528; from *Pharm. Zeit.*, 47, 82—83).—Alkaloids may be conveniently extracted from liquids in which they are partly dissolved and partly suspended, by using chloroform in a "perforation apparatus"; every trace of the alkaloid is dissolved by this means. Morphine, however, which is not readily soluble in pure chloroform, is an exception, and may be more completely extracted by precipitating with ammonia and using a mixture of chloroform with 10 per cent. of alcohol. An excess of alkali is to be avoided in the case of some alkaloids, such as veratrine and codeine. E. W. W.

**Arecoline and Arecaine.** By HANS MEYER (*Monatsh.*, 1902, 23, 22—28).—From the fact that the arecaine occurring naturally is optically inactive, and that neither synthetical arecaine nor its methyl ester (arecoline) can be resolved, it is concluded that it is 1-methyl- $\Delta^3$ -tetrahydronicotinic acid,  $\text{CH}_2\langle\begin{smallmatrix} \text{CH}_2 & \text{—} & \text{CH} \\ & \text{NMe} \cdot & \text{CH}_2 \end{smallmatrix}\rangle\text{C}\cdot\text{CO}_2\text{H}$ , and not the  $\Delta^4$ -tetrahydro-acid, which would contain an asymmetric carbon atom. Further, whilst  $\beta\gamma$ -unsaturated acids are converted into  $\alpha\beta$ -saturated acids by boiling with concentrated alkali hydroxide, arecaine undergoes no change. K. J. P. O.

**Formation of Tropine from Tropicine and Synthesis of Atropine.** By ALBERT LADENBURG (*Ber.*, 1902, 35, 1159—1162).—Details are given of the author's method (Abstr., 1890, 1333) for converting tropidine into tropine by means of hydrogen bromide, a method which has been rejected as unworkable by Willstätter (Abstr., 1901, i, 223). The separation of tropine from  $\psi$ -tropine is best effected by transformation of the bases into the aurichlorides, the tropine salt being then obtained by crystallisation from hot water. The steps in the complete synthesis of atropine are tabulated. R. H. P.

**Conium Alkaloids.** By FELIX B. AHRENS (*Ber.*, 1902, 35, 1330—1334).—A mixture of bases obtained as a residue in the manu-



facture of *d*-coniine was found to consist principally of *l*-1-methylconiine and *d*-coniine. These were separated by means of the hydrobromides, *d*-coniine hydrobromide being much the less soluble.

*l*-Methyl-1-*coniine* is a colourless liquid with an odour like coniine, boils at 175.6° under 767 mm. pressure, has a sp. gr. 0.8349 at 20°/20°, and  $[\alpha]_D - 81.92^\circ$  at 20°. The *hydrochloride* crystallises in needles melting at 191—192°; the *hydrobromide* crystallises from water in large needles, or from alcohol in leaflets melting at 189—190°, and the *hydriodide* in small, lustrous leaflets melting at 147°. The *platinichloride* separates from water in clusters of orange-coloured crystals and melts at 153—154°; the *aurichloride* crystallises in small, lustrous leaflets melting at 77—78°. The *mercurichloride*,  $C_9H_{19}N, HCl, 3HgCl_2$ , separates from water in transparent crystals which melt at 152—153°, and the *picrate* in long needles which melt at 121—122°.

The coniine may be more readily separated from the methylconiine by transformation into the nitroso-compound. The coniine obtained from the nitroso-compound is a mixture of *d*- and *i*-coniine, from which the *d*-coniine can be separated by means of its hydrogen tartrate. The *l*-coniine thus obtained boiled at 166.5° and had  $\alpha_D - 15^\circ$  at 20°. The *hydrochloride* crystallises in needles melting at 214—215°; the *hydrobromide* in silky needles melting at 205°; the *hydriodide* in needles melting at 145—146°, and the *nitrate* in needles melting at 82—83°. The *platinichloride* separates from water in red crystals melting at 160°, and the *aurichloride* in long, golden-yellow prisms melting at 59°. The coniine obtained by treatment of the methylconiine with hydrogen iodide is partially racemised. R. H. P.

**Corydalis Alkaloids.** By JOHANNES GADAMER [with H. ZIEGENBEIN and H. WAGNER] (*Arch. Pharm.*, 1902, 240, 81—113. Compare this vol., i, 306).—Corycavine (Freund and Josephy, *Abstr.*, 1892, 1367; Ziegenbein, *Abstr.*, 1897, i, 176) gave numbers on analysis which agree best with the formula  $C_{23}H_{23}O_6N$ ; it is optically inactive.

*Corycavamine*,  $C_{21}H_{21}O_5N$ , does not contain methoxyl or hydroxyl groups; it melts at 147—148° and has  $[\alpha]_D + 166.6^\circ$  in 2.23 per cent. chloroform solution at 20°. It is a monoacid base; the *hydrochloride*, *hydrobromide*, *hydriodide*, *sulphate* (with  $6H_2O$ ), *nitrate*, *aurichloride*, and *platinichloride* were analysed. When it is heated at 180° for a few minutes and the product crystallised from alcohol, it is converted into an optically inactive isomeride, *i*-corycavamine melting at 213—214°; this is certainly not identical with cryptopine.

Bulbocapnine, which contains a methoxyl group and forms a triacetyl derivative (Ziegenbein, *Abstr.*, 1897, i, 175; Herzig and Meyer, *Abstr.*, 1898, i, 53), could not be made to yield a tetramethoxy-compound by boiling this derivative with methyl alcoholic sodium methoxide; some other product was obtained. By oxidising it with  $\frac{1}{2}$  per cent. aqueous potassium permanganate, a small quantity of a crystalline product was obtained.

*Corydine* (compare Merck, *Abstr.*, 1893, i, 492),  $C_{21}H_{23}O_4N$  (or  $C_{21}H_{25}O_4N$ ), contains two methoxyl groups and reacts with acetic anhydride, yielding a product which melts at 112°, but when analysed

gives numbers difficult of interpretation. It melts at 129—130° when crystallised from ether; from dilute alcohol, it was once obtained in needles which melted and decomposed at 103—105° and probably contained water or alcohol of crystallisation. It has  $[\alpha]_D + 204.3^\circ$  in 1.56 per cent. chloroform solution at 20°. It is a monoacid base; the *hydrochloride*, *hydrobromide*, and *nitrate* were analysed.

Corytuberine (Dobbie and Lauder, *Trans.*, 1893, 63, 485) can be obtained in considerable quantity from the tubers by concentrating the extract after it has been exhausted with ether, making the residue slightly alkaline with ammonia, adding a little chloroform, and shaking; an amorphous deposit is formed which becomes crystalline after a time. The analyses agree best with the formula  $C_{19}H_{23}O_4N, 5H_2O$ , or  $C_{17}H_{15}N(OMe)_2(OH)_2$ , since two hydroxyl groups are present in addition to the two methoxyl groups. It melts and decomposes at 240° and has  $[\alpha]_D + 282.6^\circ$  in 0.198 per cent. alcoholic solution at 20°. It is a monoacid base; the *hydrochloride* (with  $[\alpha]_D 167.7^\circ$  in 1.99 per cent. solution), *hydrobromide*, *sulphate* (with  $4H_2O$ ), and *platinichloride* (with  $3H_2O$ ) were analysed; the aurichloride is very unstable. The *diacetyl* derivative crystallises from absolute alcohol with  $1C_2H_5 \cdot OH$  and melts at 72°; its *platinichloride* was analysed; its *aurichloride* melts at 195—196°. When corytuberine is heated with methyl alcoholic methyl iodide at 95°, it forms a crystalline compound which melts above 250°, but no base could be obtained from this.

C. F. B.

**Decomposition Products of *d*-Lupanine from *Lupinus Albus*.** By ARTURO SOLDAINI (*Chem. Centr.*, 1902, i, 669; from *Boll. Chim. Farm.*, 41, 37—46).—The original paper contains a description of methods of separating the bases still contained in (? crude) *d*-lupanine. In addition to the bases  $C_8H_{15}ON$  and  $C_7H_{11}ON$ , the presence of at least one other base seems to have been proved. These substances are soluble in cold water, strongly alkaline and odourless, but when treated with potassium hydroxide and a small quantity of water they all emit very similar odours.

E. W. W.

**Quinine and Cinchonidine Ethyl Carbonates.** VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 123748. Compare Abstr., 1901, i, 738, 739).—Quinine ethyl carbonate is produced by heating together crystallised quinine hydrochloride, ethyl chloroformate, pyridine, and benzene. Cinchonidine ethyl carbonate is obtained in a similar manner from cinchonidine hydrochloride.

G. T. M.

**Double Dissociation.** By EDGAR WEDEKIND and ROBERT OECHSLEN (*Ber.*, 1902, 35, 1075—1080. Compare this vol., i, 277).—The following results show that “double dissociation” only occurs in the case of quaternary bases containing a methyl group, and is therefore probably due to the “mobility” of the latter; when a hydrogen atom is present instead of a methyl radicle, the same change occurs still more readily.

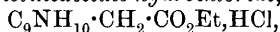
Ethyl 1-benzylpiperidiniumiodoacetate (this vol., i, 233), when heated at 193—194°, decomposes without yielding a definite product; ethyl iodoacetate is not formed. *Ethyl 1-methylpiperidiniumiodo-*

acetate,  $C_5NH_{10}MeI \cdot CH_2 \cdot CO_2Et$ , on the other hand, which separates from alcohol in colourless crystals and melts at  $158-159^\circ$ , decomposes at  $175^\circ$ , giving dimethylpiperidinium iodide and ethyl iodoacetate.

*Ethyl 1-ethyltetrahydroquinoliniumiodoacetate* forms slightly yellow crystals and decomposes at  $128-130^\circ$  without yielding a definite product; it thus differs from the corresponding methyl derivative.

Whereas ethyl 1-methyltetrahydroisoquinoliniumiodoacetate decomposes at  $160^\circ$ , forming dimethyltetrahydroisoquinolinium iodide, the analogous ethyl compound decomposes at  $110^\circ$  without yielding a crystalline product; the same is true of *ethyl 1-benzyltetrahydroisoquinoliniumiodoacetate*, which crystallises from acetone and decomposes at  $154-155^\circ$ .

*Ethyl tetrahydroquinolineacetate hydrochloride*,



crystallises in leaflets, sinters at  $90^\circ$ , melts and decomposes at  $95-97^\circ$ , and is so prone to double dissociation that it is transformed by recrystallisation from absolute alcohol or chloroform into tetrahydroquinoline hydrochloride; by water at  $0^\circ$ , it is hydrolysed into hydrochloric acid and ethyl tetrahydroquinolineacetate. W. A. D.

**Compounds of Thallic Chloride with Organic Bases.** By CARL RENZ (*Ber.*, 1902, 35, 1110-1115).—Thallic chloride forms additive compounds with organic bases when alcoholic solutions of the metallic salt and the base are mixed, and also double salts with the hydrochlorides of organic bases, which are prepared from solutions of the base and thallic chloride in hydrochloric acid, or by treatment of the additive compounds just mentioned with hydrochloric acid. Both classes of derivatives crystallise well and are not hygroscopic; water decomposes the additive compounds far more easily than the double salts. The double chlorides are converted into corresponding bromides and iodides by treatment with potassium bromide and iodide respectively. The following substances are described: with pyridine, the *thallic chloride*,  $TiCl_3 \cdot (C_5NH_5)_3$ , and *thalliiodide*,  $TI_3 \cdot C_5NH_5$ ; and the *double salts*  $(TiCl_3)_2(C_5NH_5, HCl)_3$ , melting at  $130^\circ$ , and  $(TI_3)_2(C_5NH_5, HI)_3$ ; with quinoline, the *thallic chloride*,  $TiCl_3 \cdot (C_9NH_7)_3$ , and the *double salts*,  $TiCl_3 \cdot (C_9NH_7, HCl)_2$  and  $TI_3 \cdot (C_9NH_7, HI)_2$ . The *double salt* of thallic chloride and camphylamine hydrochloride,  $TiCl_3 \cdot (C_{10}H_{17} \cdot NH_2, HCl)_2$ , crystallises in needles; that of thallic chloride and atropine hydrochloride,  $TiCl_3 \cdot C_{17}H_{23}O_3N, HCl$ , in needles, and that with hyoscyamine hydrochloride,  $TiCl_3 \cdot C_{17}H_{23}O_3N, HCl$ , is a crystalline powder.  $\beta$ -Naphthylamine hydrochloride forms a crystalline *double salt*,  $TiCl_3 \cdot (C_{10}H_7 \cdot NH_2, HCl)_3$ , whereas  $\alpha$ -naphthylamine and aniline do not form salts but react with thallic chloride.

G. K. J. P. O.

**Compounds of Thallic Chloride with Organic Bases.** By RICHARD JOS. MEYER (*Ber.*, 1902, 35, 1319. Compare Renz, preceding abstract).—A claim for priority. The difference between the results obtained by Renz and the author (compare Abstr., 1900, ii, 655) may be due to employment of different methods for the preparation of the thallic chloride compounds with the organic bases. G. T. M.

**Condensation of Formaldehyde with 2-Picoline and 2-Ethylpyridine.** By WILHELM KOENIGS and GUSTAV HAPPE (*Ber.*, 1902, 35, 1343—1349).—2-Ethylpyridine is easily prepared by the reduction of 2-picolinealkine by means of zinc dust and hydriodic acid. It is shown that the compound obtained when 2-lutidylalkine is reduced in a similar manner is 2-isopropylpyridine (compare Abstr., 1891, 1119). In the preparation of 2-picolinealkine by the condensation of 2-picoline and formaldehyde, a small quantity of 2-pyridylpropanediol,  $C_5NH_4 \cdot CH(CH_2 \cdot OH)_2$ , is formed, and can be separated by means of the easily soluble *picrate*, which crystallises in slender needles and melts at 108—110°; the *platinichloride* crystallises in small needles which blacken and melt at 144—145°. 2-Piperidylacetic acid, obtained by the oxidation of 2-pipecolylalkine by chromic acid, crystallises from alcohol in small, slender needles melting at 214° and forms a crystalline *hydrochloride* melting at 180—182°, and a *platinichloride* which melts and decomposes at 203°.

R. H. P.

**p-Nitrophenyl-2-picolyalkine and its Derivatives.** By R. KNICK (*Ber.*, 1902, 35, 1162—1163).—*p*-Nitrophenyl-2-picolyalkine (2- $\beta$ -hydroxy- $\beta$ -p-nitrophenylethylpyridine),  $NO_2 \cdot C_6H_4 \cdot CH(OH) \cdot CH_2 \cdot C_5NH_4$ , obtained by heating 2-picoline with *p*-nitrobenzaldehyde and water at 135—140° for 10 hours, crystallises from alcohol in lustrous, yellow leaflets and melts at 165°; the *platinichloride* crystallises in reddish leaflets which melt and decompose at 203°, the *aurichloride* is amorphous and melts at 105°, the *hydrochloride* crystallises in yellow leaflets melting at 215°, the *picrate* in small, yellow needles melting at 182°, and the *mercurichloride*,  $C_{13}H_{12}O_3N_2 \cdot HCl \cdot HgCl_2$ , in long, yellow needles which decompose at 169°. The *benzoyl* derivative crystallises in white needles, melts at 192—193°, and forms an amorphous *platinichloride* which decomposes at 229°. 2- $\beta$ -Hydroxy- $\beta$ -p-aminophenylethylpyridine, obtained by reducing the nitro-compound with iron and hydrochloric acid, separates from alcohol in yellowish-red crystals which melt at 135° and turn red on exposure to air; the *hydrochloride* crystallises in small, yellow needles which decompose at 190°, the amorphous *platinichloride* decomposes at 195°, the *picrate* melts at 198° and decomposes at 202°, and the *mercurichloride* crystallises from water in brownish-yellow leaflets which sinter and begin to decompose at 171°. The *ketone*,  $NO_2 \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot C_5NH_4$ , obtained when *p*-nitrophenyl-2-picolyalkine is oxidised by chromic acid, separates from alcohol or ether in yellow leaflets and melts at 160°; the *hydrochloride* crystallises in yellow leaflets melting at 218°, the *platinichloride* in red needles which melt at 181° and decompose at 187°, the *picrate* in yellow, silky needles melting at 175°, and the *mercurichloride* melts at 77°. The crystalline *oxime* melts at 152° and forms a *hydrochloride* which crystallises in yellow needles, blackens at 195°, and melts at 209°. The *phenylhydrazone* is an unstable substance which yields a *picrate* crystallising in dark yellow needles and melting at 155°.

R. H. P.

**Condensation of 4-Methyl-3-ethylpyridine with Formaldehyde.** By WILHELM KOENIGS (*Ber.*, 1902, 35, 1349—1557).—3-Ethyl-4-pyridylpropanediol,  $C_5NH_3Et \cdot CH(CH_2 \cdot OH)_2$ , obtained when

4-methyl-3-ethylpyridine is heated with a 40 per cent. solution of formaldehyde in a sealed tube for 48 hours in a water-bath, separates from ethyl acetate in colourless crystals melting at  $102-103^{\circ}$  and forms a *hydrochloride* which crystallises in colourless, lustrous laminae or needles melting at  $122^{\circ}$ , a *platinichloride* which separates from alcohol in small, compact crystals melting and decomposing at  $170^{\circ}$ , and a *picrate* which crystallises from ethyl acetate and melts at  $115-116^{\circ}$ . When oxidised with chromic acid, the diol yields 3-ethylpyridine-4-carboxylic acid, crystallises from alcohol in small, colourless needles, and melts at  $216-217^{\circ}$ .

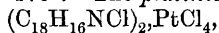
4-Methyl-3-ethylpyridine does not condense with more than 2 mols. of formaldehyde. 3-Ethylpyridyl-4-ethanol,  $C_5NH_3Et \cdot CH_2 \cdot CH_2 \cdot OH$ , obtained when methylethylpyridine is heated with an alcoholic solution of formaldehyde for 36 hours, is an oil which forms a crystalline *picrate* melting at  $110^{\circ}$  and a *platinichloride* which crystallises in flat, yellow prisms melting and decomposing at  $190-192^{\circ}$ . The corresponding piperidine compound, obtained by reduction with sodium and alcohol, is a colourless oil and forms an *aurichloride* which crystallises in broad needles and melts at  $122^{\circ}$ . R. H. P.

**Action of Benzyl Chloride and Iodide on Pyridine.** II. By A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1901, **34**, 130—133. Compare Abstr., 1901, i, 484).—The action of benzyl haloid compounds on pyridine may give rise to hydrocarbons in the following two ways: (1) By the reduction of the haloid compound, yielding the corresponding saturated hydrocarbon; (2) by the removal of hydrogen chloride from the haloid compound, giving a hydrocarbon of the ethylene series; such hydrocarbons may also be formed from the elements of two mols. of the haloid derivative.

The interaction of benzyl chloride or iodide and pyridine, whether taking place in sealed tubes or open vessels, gives rise to toluene and to stilbene. T. H. P.

**Action of Diphenylbromomethane on Pyridine.** By A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 133—137).—1-Bromo-1-diphenylmethylpyridine,  $CHPh_2 \cdot C_5NH_3Br$ , prepared by the action of diphenylbromomethane on pyridine, separates from aqueous alcohol in prismatic crystals containing  $1H_2O$  and melting at  $129-130^{\circ}$ ; it is readily soluble in water, alcohol, or acetone.

When treated with sodium picrate, the above compound yields 1-diphenylmethylpyridone picrate,  $CHPh_2 \cdot C_5NH_3 \cdot O \cdot C_6H_2(NO_2)_3$ , which separates from water, alcohol, or acetone in very slender needles melting and decomposing at  $173-175^{\circ}$ . The *platinichloride*,



is deposited from aqueous solution in golden scales melting at  $195^{\circ}$ .

When heated together in a sealed tube, diphenylbromomethane and pyridine give rise to diphenylmethane, tetraphenylethylene, and diphenylpyridylmethane,  $CHPh_2 \cdot C_5NH_4$ ; the last is probably a mixture of isomerides. T. H. P.

**Action of Triphenylchloromethane and Triphenylbromomethane on Pyridine.** By A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 137—140).—Triphenylbromomethane reacts

energetically with dry pyridine, yielding bromodiphenylmethylpyridine (see preceding abstract), which under the action of the moisture of the air undergoes partial decomposition into triphenylcarbinol and pyridine hydrobromide.

The compound,  $\text{CPh}_3 \cdot \text{OH} \cdot \text{C}_5\text{NH}_5$ , obtained by the direct action of pyridine on triphenylcarbinol, is extremely soluble in benzene and is decomposed into its constituents on continuous heating at  $80^\circ$ .

Triphenylchloromethane has no apparent action on oxypyridine, but in the presence of moisture and excess of pyridine a reaction takes place similar to that obtained with the bromo-compound.

When heated with pyridine in sealed tubes, triphenylchloromethane or triphenylbromomethane yields triphenylmethane, together with an oily compound and basic products.

T. H. P.

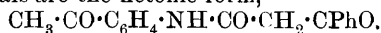
**Preparation of Indoles from Pyrroles.** By MAXIMILIAN DENNSTADT (D.R.-P. 125489. Compare Dennstadt and Voigtländer, Abstr., 1894, i, 259).—Indole is obtained by dissolving pyrrole in 10 per cent. sulphuric acid, allowing the product to remain for 1—2 hours, and then distilling the mixture with excess of sodium hydroxide in a current of steam.

Diethylindole, prepared from ethylpyrrole by a similar process, is a viscid oil with a disagreeable odour; it boils at  $270\text{--}310^\circ$  under the ordinary pressure.

G. T. M.

**Synthesis of 2- and 4-Hydroxyquinolines.** By RUDOLF CAMPS (*Arch. Pharm.*, 1902, 240, 135—146).—Phenacetyl-*o*-aminoacetophenone,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2\text{Ph}$ , on condensation yields a 2-hydroxyquinoline without any admixture of 4-isomeride (this vol., i, 178). This is evidently due to the negative character of the phenyl group; a similar result is obtained when this group is replaced by the groups  $\text{CPhO}$ ,  $\text{CMeO}$ ,  $\text{CO}_2\text{Et}$ , or  $\text{CN}$ , as will be seen below. It was not always possible to isolate the anilide, however; direct condensation to the quinoline often took place.

When *o*-aminoacetophenone is boiled for a little while, or heated for half-an-hour at  $190\text{--}200^\circ$  with ethyl benzoylacetate, 3-benzoyl-2-hydroxy-4-methylquinoline is at once formed. This melts at  $264^\circ$ ; it has hardly any basic character; it forms a sodium salt, but it does not give any coloration with ferric chloride. If the two substances are heated only at  $140\text{--}145^\circ$  for half-an-hour, the main product is benzoylacetetyl-*o*-acetanilide; this melts at  $74\text{--}75^\circ$  when crystallised from light petroleum; from benzene, it crystallises with some of the solvent and then melts at  $65^\circ$ . In alcoholic solution, it gives a violet coloration with ferric chloride, and so must be the enolic form,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH} \cdot \text{CPh} \cdot \text{OH}$ . If the alcoholic solution is boiled, even for a few minutes only, it gives the ferric chloride reaction no longer; the crystals obtained from it then melt at  $176^\circ$ , losing water at the same time and forming the quinoline derivative; evidently these crystals are the ketonic form,



If the enolic form melting at  $75^\circ$  is suspended in alcohol and the solution allowed to remain for some time, reddish crystals are formed, less

soluble in ether and melting at  $104^{\circ}$ ; these also give the ferric chloride reaction, and presumably represent a second enolic form geometrically isomeric with the first.

Aminoacetophenone and ethyl acetoacetate yield only 3-*acetyl-2-hydroxy-4-methylquinoline*, which melts at  $267^{\circ}$ . Some anilide seemed to be formed, but it could not be isolated.

When aminoacetophenone and ethyl malonate are mixed and heated to boiling repeatedly, the main product is the *acetanilide* of 2-*hydroxy-4-methylquinoline-3-carboxylic acid*; this melts at  $275^{\circ}$  and is very stable towards alkalis, but is hydrolysed to the acid when it is heated for some time with fairly concentrated sulphuric acid. If the ketone and malonate are heated only at  $170-175^{\circ}$  for half-an-hour, there are formed in addition *ethyl acetylphenylmalonamate* (*ethyl malonate mono-acetanilide*),  $\text{COMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , which is the main product, and symmetrical *diacetylphenylmalonamide* (*diacetanilide malonic acid*),  $\text{CH}_2(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{COMe})_2$ . The first of these is soluble in ether and melts at  $55^{\circ}$ ; with sodium in ethereal solution, it yields a sodio-derivative. When boiled for some time with a solution of sodium hydroxide in dilute alcohol, it forms 2-*hydroxy-4-methylquinoline-3-carboxylic acid*, which melts at  $254-255^{\circ}$ , losing carbon dioxide and leaving 2-*hydroxy-4-methylquinoline*; if the boiling is continued only for a short time, the *ethyl ester* of this acid is obtained melting at  $251-252^{\circ}$ ; this is also formed spontaneously from the sodio-derivative by loss of sodium hydroxide. The diacetylphenylmalonamide is insoluble in ether but soluble in benzene, unlike the anilide melting at  $275^{\circ}$ ; it melts at  $159-160^{\circ}$ , losing water and forming the anilide just mentioned; boiling with dilute alcoholic sodium hydroxide also effects this conversion.

When aminoacetophenone and ethyl cyanoacetate are heated together at  $200^{\circ}$  for half-an-hour, 3-*cyano-2-hydroxy-4-methylquinoline* is formed; it melts at  $320^{\circ}$ , forms a sodium salt, and is stable to dilute acids and alkalis, but is hydrolysed to 2-*hydroxy-4-methylquinoline-3-carboxylic acid* when it is heated with strong sulphuric acid and a little water at  $130-140^{\circ}$ .

No success attended attempts to introduce halogens into the 3-position in the quinoline molecule by means of the corresponding acid chlorides. Aminoacetophenone and chloroacetyl chloride in ethereal solution give chloroacetyl aminoacetophenone melting at  $81^{\circ}$ , but boiling with a slight excess of aqueous sodium hydroxide converts this into 2:3-dihydroxy-4-methylquinoline, the chloride being eliminated.

C. F. B.

**8-Quinolinealdehyde.** By JOH. HOWITZ (*Ber.*, 1902, 35, 1273-1275).—8-*Iodomethylquinoline*,  $\text{C}_9\text{H}_6\text{N}\cdot\text{CH}_2\text{I}$ , prepared by the action of methyl iodide on the bromo-compound, crystallises from alcohol in colourless needles and melts at  $84^{\circ}$ .

8-*Quinolinealdehyde*,  $\text{C}_9\text{H}_6\text{N}\cdot\text{CHO}$ , prepared by oxidising the preceding compound with nitric acid (sp. gr. 1.3), crystallises from aqueous alcohol in long, white, glistening needles, melts at  $94-95^{\circ}$ , and is volatile with steam. The *platinichloride*,  $2\text{C}_{10}\text{H}_7\text{ON}\cdot\text{H}_2\text{PtCl}_6$ , is a reddish-yellow, crystalline powder, can be recrystallised from hot

alcoholic hydrochloric acid, and melts and decomposes at 250°. The aldehyde forms a bisulphite compound, an oxime, hydrazine, and anilino-derivative, reduces ammoniacal silver solutions, and on oxidation yields quinoline-8-carboxylic acid. T. M. L.

**Products of Condensation of Tetramethyldiaminobenzhydrol with Primary Aromatic Amines, in which the Para-position is Occupied.** By ALFRED GUYOT and M. GRANDERYE (*Compt. rend.*, 1902, 134, 549—551).—With the object of preparing triphenylmethane derivatives, *p*-nitroaniline and tetramethyldiaminobenzhydrol were heated together at 100° in the presence of hydrochloric acid; *p*-nitrophenyl-leucauramine (Möhlau and Heinze, this vol., i, 243) is first formed, and on prolonged heating is converted into *p*-dimethylaminobenzylidene-*p*-nitroaniline,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ ; the latter crystallises in dichroic, orange plates melting at 198—199°; the hydrochloride forms violet needles melting at 193°.

With sulphanilic acid and the benzhydrol, no leucauramine is formed, the reaction leading to the direct formation of *p*-dimethylaminobenzylidene-*p*-aminobenzenesulphonic acid; *p*-phenylenediamine and the benzhydrol behave in a similar manner. K. J. P. O.

**Sulphonic and Carboxylic Acids of the *as*-Dialkyl-*p*-phenylenediamines.** KALLE & Co. (D.R.-P. 124907).—The sulphonic and carboxylic acids of the dialkyl-*p*-phenylenediamines are produced by heating 5-nitro-2-chlorobenzoic acid or 4-nitro-1-chlorobenzene-6-sulphonic acid with aqueous solutions of the aliphatic secondary amines, and subsequently reducing the resulting nitroamines.

4-Nitrodimethylaniline-6-sulphonic acid, produced by heating together 4-nitro-1-chlorobenzene-6-sulphonic acid and dimethylamine in aqueous solution, yields 4-aminodimethylaniline-6-sulphonic acid when reduced with iron and acetic acid; this separates from water in lustrous crystals, develops an intense red coloration with ferric chloride, and gives rise to a blue colouring matter on oxidation with sodium thiosulphate in the presence of dimethylaniline.

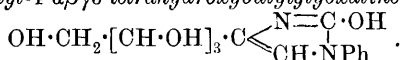
4-Nitrodimethylaniline-6-carboxylic acid, prepared from 5-nitro-2-chlorobenzoic acid, crystallises in golden-yellow needles, and when reduced gives 4-aminodimethylaniline-6-carboxylic acid, a compound separating from alcohol in grey crystals melting at 178°.

G. T. M.

**Dihydroxyketoethylenedinaphthylaminedisulphonic Acid.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 126443).—1 : 1'-Dihydroxy-6 : 6'-ketoethylenedinaphthylamine-3 : 3'-disulphonic acid,  $\text{OH} \cdot \text{C}_{10}\text{H}_5(\text{SO}_3\text{H}) \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_5(\text{SO}_3\text{H}) \cdot \text{OH}$ , obtained by treating an alkaline solution of sodium 6-amino- $\alpha$ -naphthol-3-sulphonate with chloroacetyl chloride or the corresponding bromide, separates from the acidified product as a grey powder which readily dissolves in hot water; its sodium salt is very soluble, and is only partially precipitated on the addition of sodium chloride. The acid yields a yellow nitroso-compound on treatment with nitrous acid. G. T. M.



**Method for the Detection of Glucosamine and its Employment on the Decomposition Products of Mucins.** By H. STEUDEL (*Zeit. physiol. Chem.*, 1902, **34**, 353—384. Compare Abstr., 1901, i, 674).—The product obtained by the condensation of glucosamine with phenylcarbimide does not reduce Fehling's solution, and is probably *2-hydroxy-1-phenyl-4-αβγδ-tetrahydroxybutylglyoxaline*,



One part of the compound dissolved in 156·25 parts of water at the ordinary temperature and its solubility in alcohol is even less; it has  $[\alpha]_D +76\cdot9^\circ$  at  $20^\circ$ .

Glucosamine and phenylcarbimide react in alkaline solution, yielding a sparingly soluble additive product. This has not been obtained in a pure state, but when boiled for some time with acetic acid it loses water and yields the above iminazole (glyoxaline) derivative. As the additive products of amino-acids with phenylcarbimide are only formed in acid solution, this affords a simple method for the separation of glucosamine and amino-acids.

Glucosamine added to the products formed by the acid hydrolysis of proteids is readily precipitated by the phenylcarbimide method. The compounds with reducing properties obtained from submaxillary mucin and paramucin by hydrolysis with dilute acids contain no simple glucosamine and do not combine with phenylcarbimide. When, however, the reducing compound from paramucin is boiled with concentrated hydrochloric acid, glucosamine is formed and may be precipitated by the aid of phenylcarbimide.

J. J. S.

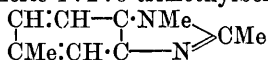
**Benziminazoles.** By OTTO FISCHER and MORITZ RIGAUD (*Ber.*, 1902, **35**, 1258—1265. Compare this vol., i, 188).—The iodide,

$\text{C}_6\text{H}_4\begin{array}{c} \text{NMe} \\ \text{NMeI} \end{array}\text{CH}$ , obtained by methylating benziminazole is converted by freshly precipitated silver chloride into the analogous chloride, which crystallises from water in slightly yellow needles, with  $1\text{H}_2\text{O}$ , and melts when dry at  $240^\circ$ ; the same salt is obtained from the carbinol base melting at  $75^\circ$  (Abstr., 1901, i, 413). On adding moist silver oxide to a solution of the methochloride, the ammonium base is formed, which is strongly alkaline and insoluble in ether; on boiling the solution, or on adding a little alkali, it is changed into the carbinol base which can be extracted with ether. Like ammonia, the ammonium base dissolves silver oxide, and on evaporating the solution silver is precipitated and N-dimethylphenylenecarbamide formed by the oxidation of the carbinol base.

*4-Nitro-3-methylaminotoluene*,  $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NHMe}$ , obtained by heating *p*-nitro-*m*-tolyl methyl ether (Reissert, Abstr., 1898, i, 315) with 33 per cent. aqueous methylamine for 4—5 hours at  $160^\circ$ , crystallises from dilute methyl alcohol in brownish-yellow prisms, melts at  $83^\circ$ , and yields, on reduction with tin and hydrochloric acid, a base which combines with boiling glacial acetic acid to form 1:2:6-*trimethylbenziminazole*,  $\begin{array}{c} \text{CMe}\cdot\text{CH}\cdot\text{C}\cdot\text{NMe} \\ \text{CH}=\text{CH}\cdot\text{C}-\text{N} \end{array}\text{CMe}$ ; this crystallises from light petroleum in colourless prisms, melts at  $122\text{—}123^\circ$ , and yields a

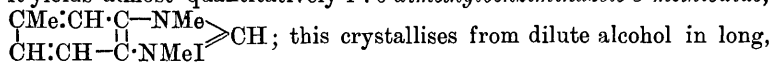
f f 2

*platinichloride* (with  $2\text{H}_2\text{O}$ ) decomposing at  $259^\circ$ , and an *aurichloride* melting at  $189\text{--}190^\circ$ ; the *mercurichloride* forms long, white needles melting at  $203\text{--}204^\circ$ , and the *picrate* yellow prisms melting at  $232\text{--}233^\circ$ . The isomeric 1 : 2 : 5-trimethylbenziminazole,

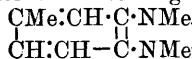


(Abstr., 1893, i, 283), crystallises from water as a hydrate and then melts at  $100^\circ$ ; when dry, it melts at  $140^\circ$ ; the *picrate* forms yellow needles or stout prisms melting at  $259\text{--}260^\circ$ , and the *platinichloride* yellow plates (with  $2\text{H}_2\text{O}$ ) melting at  $251^\circ$ ; the *aurichloride* crystallises in needles and melts at  $130\text{--}131^\circ$ , and the *mercurichloride* melts at  $199\text{--}200^\circ$ .

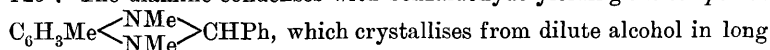
[With ERNST BECKER.]—On heating 6-methylbenziminazole obtained from 3 : 4-tolylendiamine and formic acid for 4 to 5 hours at  $140\text{--}150^\circ$  with methyl alcohol (2 mols.) and methyl iodide (2 mols.), it yields almost quantitatively 1 : 6-dimethylbenziminazole-3-methiodide,



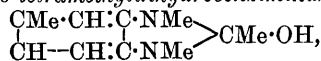
this crystallises from dilute alcohol in long, transparent needles, melts at  $227^\circ$ , and is transformed by silver chloride into the analogous *methochloride* which melts at  $275^\circ$  and is identical with the chloride from the carbinol base (*infra*). On decomposing the chloride, or better, the iodide, with moist silver oxide, an alkaline solution of the ammonium base is given, which, on adding alkali, yields the *carbinol* base,



this crystallises from benzene in stout needles, melts at  $110^\circ$ , and yields only salts of the ammonium type; the *aurichloride* melts at  $160^\circ$ , the *platinichloride* at  $262^\circ$ , and the *mercurichloride* at  $220^\circ$ . On oxidation with potassium permanganate, the carbinol yields N-dimethyltolylencarbamide which melts at  $106^\circ$  (Pinnow and Sämann, Abstr., 1899, i, 943, give  $103\text{--}104^\circ$ ). On hydrolysing either the foregoing carbinol base or the original methiodide with boiling aqueous sodium hydroxide, 3 : 4-dimethylaminotoluene,  $\text{C}_6\text{H}_3\text{Me}(\text{NHMe})_2$ , is obtained as an oil which boils at  $259\text{--}260^\circ$  under 740 mm. pressure, and yields a *hydrochloride* crystallising in thick, colourless needles and melting at  $125^\circ$ . The diamine condenses with benzaldehyde yielding the compound



which crystallises from dilute alcohol in long needles and melts at  $88^\circ$ ; the analogous derivative,  $\text{C}_{16}\text{H}_{18}\text{ON}_2$ , of salicylaldehyde crystallises from dilute alcohol in yellow cubes and melts at  $185^\circ$ . When boiled with formic acid, the diamine yields the carbinol (m. p.  $110^\circ$ ) from which it was obtained; with acetic acid, it yields 2-hydroxy-1 : 2 : 3 : 6-tetramethyldihydrobenziminazole,



which crystallises from light petroleum and melts at  $148^\circ$ .

1-Ethyl-6-methylbenziminazole-3-ethiodide, obtained by heating the 6-methylbenziminazole with ethyl iodide and absolute alcohol for 10—12 hours at  $150^\circ$ , crystallises from alcohol in colourless needles and melts at  $129^\circ$ . The derived *carbinol* is a yellow oil which yields on

hydrolysis 3:4-diethylaminotoluene as a thick oil giving a crystalline hydrochloride. W. A. D.

**Derivatives of Cinchomeronic Acid.** By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1902, 35, 1358—1367).—An attempt to prepare 2:7-benzodiazine,  $\begin{array}{c} \text{N} - \text{CH} = \text{C} \cdot \text{CH} : \text{N} \\ | \qquad \qquad | \\ \text{CH} \cdot \text{CH} : \text{C} \cdot \text{CH} : \text{CH} \end{array}$ , for which the name *copyrine* is proposed.

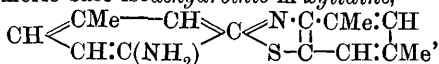
The potassium derivative of cinchomeronimide, which separates in lustrous, silvery laminae when alcoholic potash is added to an alcoholic solution of the imide, reacts with ethyl chloroacetate, forming *ethyl cinchomeronylglycine*,  $\text{C}_5\text{NH}_3 \cdot (\text{CO})_2 \cdot \text{N} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , which crystallises in small, glistening needles and melts at  $101^\circ$ .

The glycine condenses with sodium methoxide, forming *methyl 1:4-dioxycopyrinedicarboxylate*,  $\text{C}_5\text{NH}_3 \cdot \begin{array}{c} \text{CO} - \text{NH} \\ | \qquad \qquad | \\ \text{C}(\text{OH}) : \text{C} \cdot \text{CO}_2\text{Me} \end{array}$ , which crystallises from a large quantity of water in bright yellow, flat, pointed needles melting and decomposing at  $150^\circ$ . When treated with hydrogen bromide or iodide in a reflux apparatus, it yields salts of

*1:4-dioxycopyrine*,  $\text{C}_5\text{NH}_3 \cdot \begin{array}{c} \text{CO} \cdot \text{NH} \\ | \qquad \qquad | \\ \text{CO} \cdot \text{CH}_2 \end{array}$ , from which the unstable base was obtained in the form of grey laminae or pale yellow needles decomposing at about  $195^\circ$ ; the *hydrochloride*, *hydrobromide*, and *hydroiodide* crystallise in orange-yellow laminae, the *platinichloride* in orange-red needles decomposing at above  $200^\circ$ , and the *picrate* in orange-yellow needles or plates which sinter and decompose at  $195^\circ$ . When the base is treated with hydriodic acid under pressure, it is decomposed with the formation of 4-ethylpyridine-3-carboxylic acid, which crystallises from ethyl acetate in compact needles melting at  $136$ — $136.5^\circ$  and forms an *aurichloride* crystallising in lustrous, golden laminae and a *picrate* crystallising in long, lemon-coloured needles.

These derivatives of copyrine are all soluble in alkalis; such solutions, however, are readily oxidised by air or potassium persulphate yielding a red base,  $\text{C}_{10}\text{H}_{10}\text{O}_4\text{N}_4$  (?), which forms a *hydrochloride* crystallising in orange-coloured, pointed needles. R. H. P.

**Isomerides of the Base of the Dye "Erika."** By GUSTAV SCHULTZ and M. TICHOMIROFF (*J. pr. Chem.*, 1902, [ii], 65, 150—160).—The dye "Erika" (sodium methylbenzenylaminothio-xyleneazo- $\alpha$ -naphtholdisulphonate) is obtained by coupling dehydrothio-*m*-xylidine,  $\text{NH}_2 \cdot \text{C} \begin{array}{c} \text{CMe} \cdot \text{CH} \\ \text{CH} = \text{CH} \end{array} \text{C} \begin{array}{c} \text{N} \cdot \text{C} \cdot \text{CMe} : \text{CH} \\ | \qquad \qquad | \\ \text{S} - \text{C} - \text{CH} : \text{CMe} \end{array}$ , with  $\alpha$ -naphthol- $\epsilon$ -disulphonic acid. In the preparation of the base by heating *m*-xylidine with sulphur, the isomeric base isodehydrothio-*m*-xylidine,

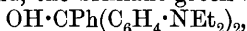


is also obtained, but forms no azo-dyes of technical value. Two attempts have been made to convert this second base into the Erika base. The first consisted of (i) diazotisation, by which a *diazochloride* melting and decomposing at  $80$ — $90^\circ$  was obtained; (ii) replacement

of the diazo-group by hydrogen, the resulting *m*-methylbenzenyl-*p*-amino-*m*-thio-xylénol being a substance which crystallises in yellow needles melting at 74·5; (iii) nitration of the thio-xylénol, by which two mononitro-derivatives melting at 152° and 146° respectively were obtained; (iv) reduction of the former (m. p. 152°), by which a base was obtained which crystallised in small, lustrous, red needles, and melted at 95°, but was not identical with the Erika base and did not yield any useful azo-dyes. The second attempt consisted of (i) nitration of the base by which a mononitro-derivative was obtained, which crystallised in yellow-red needles melting at 192°; (ii) diazotisation of the nitro-derivative (m. p. 192°); (iii) replacement of the diazo-group by hydrogen, by which the above-mentioned nitro-derivative (m. p. 146°) of the thio-xylénol was obtained, (iv) reduction of the nitro-derivative (m. p. 146°), by which a reddish base was obtained, which crystallises in slender, reddish needles melting at 89°, but was not identical with the Erika base.

R. H. P.

**Etherification of Carbinols by Alcohols.** By OTTO FISCHER and KARL WEISS (*Chem. Centr.*, 1902, i, 471; from *Zeit. Farben. u. Textilchem.*, 1902, 1, 1—3. Compare Abstr., 1901, i, 82).—*o*-Aminobenzyl alcohol and triphenylcarbinol cannot be induced to etherify with ethyl or benzyl alcohol either by prolonged boiling or by heating at 150°, whilst, on the other hand, the brilliant green base,



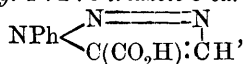
the crystal-violet base,  $\text{OH} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_3$ , and tetramethyldiaminobenzhydrol,  $\text{OH} \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , readily form ethers when boiled with these alcohols, and even react slowly with them in the cold. The ethers thus obtained resemble those of the malachite-green base in being colourless in the solid state or in solutions free from acids, but are hydrolysed and turned blue by the action of even weak acids such as carbonic or acetic acid. The violet base combines with phenol to form an additive compound,  $\text{OH} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_3 \cdot 3\text{PhOH}$ , which crystallises from a mixture of benzene and light petroleum in needles, melts at about 120°, and is readily soluble in alcohol or benzene, forming a blue solution, but only slightly so in ether or light petroleum. The methyl ether of the crystal-violet base,  $\text{C}_{26}\text{H}_{33}\text{ON}_3$ , separates from light petroleum in colourless crystals, melts at 158—159°, and is very readily soluble in benzene or ether, but less so in alcohol or light petroleum. The ethyl ether,  $\text{C}_{27}\text{H}_{35}\text{ON}_3$ , melts at 143—144°. The benzyl ether,  $\text{C}_{32}\text{H}_{37}\text{ON}_3$ , crystallises from light petroleum, melts at 174—175°, and is readily soluble in ether or benzene. The methyl ether of tetramethyldiaminobenzhydrol,  $\text{C}_{18}\text{H}_{24}\text{ON}_2$ , melts at 71—72° and is rather soluble in alcohol, ether, or benzene, but less so in light petroleum. The ethyl ether forms an oil which is easily soluble in ether, alcohol, or benzene, but less so in light petroleum; after remaining several months, this oil deposits crystals of the anhydride of tetramethyldiaminobenzhydrol,  $\text{C}_{34}\text{H}_{42}\text{ON}_4$ , which may be crystallised from a mixture of benzene and light petroleum, melts at 200—201°, and is hydrolysed by boiling with dilute acids regenerating the hydrol. The benzyl ether of tetramethyldiaminobenzhydrol,  $\text{C}_{24}\text{H}_{28}\text{ON}_2$ , crystallises in four-sided plates and melts at 102—103°.

E. W. W.

**Synthesis of Derivatives of 1:2:3-Triazole.** By OTTO DIMROTH (*Ber.*, 1902, 35, 1029—1038).—1-Phenyl-5-methyl-1:2:3-triazole-4-

carboxylic acid,  $\text{NPh} \begin{smallmatrix} \text{N}=\text{N} \\ \text{CMe}:\text{C} \end{smallmatrix} \cdot \text{CO}_2\text{H}$ , prepared by the action of phenylazoimide on ethyl acetoacetate in presence of sodium ethoxide, crystallises from water in prismatic needles and from benzene in scales and melts at  $148^\circ$ ; the *potassium* salt crystallises in flakes from dilute alcohol; the *ammonium* salt separates from alcohol in a crystalline crust; the *copper* salt forms blue prisms. The *methyl* ester,  $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_3$ , crystallises from methyl alcohol in glistening flakes and melts at  $73-74^\circ$ ; the *ethyl* ester,  $\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}_3$ , crystallises from a mixture of ether and light petroleum in flakes and melts at  $60^\circ$ .

1-Phenyl-5-methyl-1:2:3-triazole,  $\text{NPh} \begin{smallmatrix} \text{N}=\text{N} \\ \text{CMe}:\text{CH} \end{smallmatrix}$ , prepared by heating the dry acid, crystallises from light petroleum in flakes, from dilute alcohol in prisms, melts at  $64^\circ$ , is not readily volatile with steam, exhibits basic properties, dissolves in hydrochloric acid, and forms a platinichloride. 1-Phenyl-1:2:3-triazole-5-carboxylic acid,



prepared by oxidising the preceding compound with potassium permanganate, crystallises from alcohol in needles and melts at  $176^\circ$ , liberating carbon dioxide; the *potassium* salt crystallises from alcohol in needles; the *barium* salt,  $\text{C}_{18}\text{H}_{12}\text{O}_4\text{N}_6\text{Ba} \cdot 2\text{H}_2\text{O}$ , crystallises from water in needles; the *copper* salt forms blue prisms and is insoluble in water; the *methyl* ester,  $\text{C}_{10}\text{H}_9\text{O}_2\text{N}_3$ , crystallises from dilute methyl alcohol in minute needles and melts at  $101^\circ$ ; the *ethyl* ether crystallises from light petroleum in long needles and melts at  $54-55^\circ$ ; the *amide*,  $\text{C}_9\text{H}_8\text{ON}_4$ , crystallises from water in prisms and melts at  $146^\circ$ ; when heated, the acid is converted into 1-phenyl-1:2:3-triazole (Michael, Luehn, and Higbee, *Abstr.*, 1898, i, 496).

1-Phenyl-1:2:3-triazole-4:5-dicarboxylic acid (Zincke and Petermann, *Abstr.*, 1901, i, 106) is formed on oxidising 1-phenyl-5-methyl-1:2:3-triazole-4-carboxylic acid. When cautiously heated alone, or when heated with water at  $130-140^\circ$ , it is converted into 1-phenyl-

1:2:3-triazole-4-carboxylic acid,  $\text{NPh} \begin{smallmatrix} \text{N}=\text{N} \\ \text{CH}:\text{C} \end{smallmatrix} \cdot \text{CO}_2\text{H}$ ; this crystallises from methyl alcohol in prisms with  $1\text{MeOH}$ , which is given off at  $100^\circ$ , and melts at  $151^\circ$ ; the *copper* salt forms small, blue prisms; the *methyl* ester crystallises from methyl alcohol in prisms and melts at  $121^\circ$ .  
T. M. L.

**Isomerism of the  $\alpha$ -Triazole Compounds.** By OTTO DIMROTH (*Ber.*, 1902, 35, 1038—1047).—1-Nitrophenyl-1:2:3-triazole-5-car-

boxylic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \begin{smallmatrix} \text{N}=\text{N}=\text{N} \\ \text{C}(\text{CO}_2\text{H}):\text{CH} \end{smallmatrix}$ , prepared by nitrating phenyltriazolecarboxylic acid, crystallises from spirit in minute, colourless needles and melts at  $176^\circ$ . 1-Aminophenyl-1:2:3-triazole-5-carboxylic acid hydrochloride,  $\text{C}_9\text{H}_9\text{O}_2\text{N}_4\text{Cl}$ , crystallises from hydrochloric acid in colourless, obliquely-truncated prisms; it is oxidised by alkaline

permanganate to an acid identical with Pechmann's *o*-triazolecarboxylic acid (Abstr., 1891, 1117), and this acid, when heated at 225°, gave Pechmann's *o*-triazole.

1-Nitrophenyl-1:2:3-triazole-4-carboxylic acid crystallises from alcohol in prismatic needles. The hydrochloride of the amino-acid crystallises from dilute hydrochloric acid in colourless needles, melts at 200—202°, and is less soluble than the isomeride described above. Like the isomeride, it is oxidised to Pechmann's triazolecarboxylic acid, and the latter, when heated, is converted into Pechmann's crystalline triazole.

Contrary to the statement of Bladin (Abstr., 1894, i, 176), only one of the three carboxylic acids,  $\text{NH} \begin{array}{c} \text{N} \cdot \text{C} \cdot \text{CO}_2\text{H} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{CH} \end{array}$ ,  $\text{N} \begin{array}{c} \text{N} - \text{C} \cdot \text{CO}_2\text{H} \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{CH} \end{array}$ , and  $\text{N} \begin{array}{c} \text{N} - \text{CH} \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{C} \cdot \text{CO}_2\text{H} \end{array}$  and only one of the triazoles,  $\text{NH} \begin{array}{c} \text{N} \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{CH} \end{array}$  and  $\text{N} \begin{array}{c} \text{N} - \text{CH} \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{CH} \end{array}$  is capable of existing in a stable form. T. M. L.

**Action of Hydrazobenzene and its Substitution Derivatives on Aldehydes.** By BERTHOLD RASSOW and KURT RÜLKE (*J. pr. Chem.*, 1902, [ii], 65, 97—122).—Benzaldehyde condenses with hydrazobenzene in the presence of acetic acid, forming dibenzylidenebenzidine. 2:4:6-Picrylphenylhydrazine, when warmed with an alcoholic solution of formaldehyde, yields 2:4-dinitro-6-nitrosoazobenzene. 4-Methylhydrazobenzene, when warmed with an alcoholic solution of formaldehyde, yields a compound which crystallises in white laminae, melts at 190—193°, and is one of the two possible di-*p*-methyltetraphenylhexahydrotetrazines. *p*-Hydrazotoluene, in a similar manner, yields either (a) 1:2:4:5-tetra-*p*-tolylhexahydro-1:2:4:5-tetrazine,

$\text{CH}_2 \cdot [\text{N}(\text{C}_6\text{H}_4\text{Me}) \cdot \text{N}(\text{C}_6\text{H}_4\text{Me})]_2 \cdot \text{CH}_2$ , which crystallises in yellowish, thin, monoclinic laminae, melts at 213—214°, and is decomposed by mineral acids, or (b) methylenedi-*p*-hydrazotoluene,  $\text{CH}_2[\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{N}(\text{C}_6\text{H}_4\text{Me})]_2$ , which crystallises from petroleum in small, monoclinic plates and melts at 156°. The analogous 1:2:4:5-tetra-*p*-tolyl-3:6-dimethylhexahydro-1:2:4:5-tetrazine was obtained from acetaldehyde and crystallises in yellowish, rhombic prisms, which melt at 150—151°. The corresponding tetrazine from *o*-hydrazotoluene and formaldehyde crystallises in small, colourless, rhombic needles, which melt and decompose at 187—188°, and the tetrazine from *m*-hydrazotoluene and formaldehyde in colourless rhombic needles which melt at 166·5—167·5°. R. H. P.

**Reduction of Nitroaldehyde Hydrazones.** By EUGEN BAMBERGER and JOHANNES FREI (*Ber.*, 1902, 35, 1084—1093).—Ammonium sulphide readily reduces nitroaldehydrazones to arylhydrazoaldoximes of the type  $\text{NHAr} \cdot \text{NH} \cdot \text{CR} \cdot \text{N} \cdot \text{OH}$ ; it is probable that nitronic acids (this vol., i, 246),  $\text{Ar} \cdot \text{N} \cdot \text{N} \cdot \text{CR} \cdot \text{NO} \cdot \text{OH}$ , are first formed, and that these then undergo reduction to the oximes.

*Phenylhydrazoformaldoxime*,  $\text{NHPh} \cdot \text{NH} \cdot \text{CH} \cdot \text{N} \cdot \text{OH}$ , obtained by passing dry hydrogen sulphide at a temperature not exceeding 40°,

into an absolute alcoholic solution of  $\alpha$ -nitroformaldehyde phenylhydrazone saturated with ammonia at  $0^\circ$ , crystallises from alcohol in white, lustrous needles and decomposes at  $113.5^\circ$ ; it cannot be crystallised from hot solvents, and is converted by warm dilute mineral acids initially into formic acid, hydroxylamine, and phenylhydrazine, the last two interacting to form ammonia and a diazonium salt which ultimately yields phenol. Using  $\alpha$ -nitroformaldehyde phenylhydrazone for the reduction, a considerable quantity of formazyl mercaptan is produced, but this is obviated and the yield of the hydrazoformaldoxime increased by employing the  $\beta$ -hydrazone. *Phenylazoformaldoxime*,  $N_2Ph \cdot CH : N \cdot OH$ , obtained by oxidising the hydrazo-compound with aqueous ferric chloride at  $0^\circ$ , crystallises from light petroleum in golden, felted needles, melts and decomposes at  $94^\circ$ , and is much more stable towards boiling water than the parent substance; it is, however, decomposed like the latter by warm dilute mineral acids.

Phenylhydrazoacetaldoxime, and *p*-chloro-, 2 : 4-dichloro-, and 2 : 4 : 6-trichloro-phenylhydrazoacetaldoxime (this vol., i, 247) were obtained in good yield by reducing the corresponding nitroacetaldoximes.

*Phenylazobenzaldoxime*,  $N_2Ph \cdot CPh : N \cdot OH$ , crystallises from a mixture of benzene and light petroleum in orange-yellow needles with a bronze-like lustre, and melts and decomposes at  $134-135^\circ$  (corr.).

*Phenylhydrazopropionaldoxime*,  $NHPh \cdot NH \cdot CEt : N \cdot OH$ , obtained from nitropropionaldehyde phenylhydrazone, crystallises from benzene on adding light petroleum in lustrous needles and melts at  $87.5-88^\circ$ ; *phenylazopropionaldoxime* crystallises from light petroleum in radial aggregates of golden, silky needles and melts at  $77.5-78^\circ$ .

*Phenylhydrazovaleraldoxime*, prepared from nitrovaleraldehyde phenylhydrazone, forms white, silky needles melting and decomposing at  $100.5-101^\circ$ , and yields an azo-compound which crystallises from light petroleum or dilute alcohol in yellow, silky needles and melts at  $103-103.5^\circ$ .

W. A. D.

**Certain Properties of Azobenzene and Hydrazobenzene.** By PAUL FREUNDLER and L. BÉRANGER (*Compt. rend.*, 1902, 134, 465-467).—Friedel and Crafts' reaction cannot be employed in preparing azo-ketones and azo-aldehydes by the action of acyl chlorides and aluminium chloride or bromide on azobenzene or diacetylhydrazobenzene, for these compounds simply form insoluble additive products with the aluminium salt but undergo no further change.

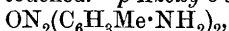
On acetylating a sample of hydrazobenzene containing azobenzene with acetic anhydride, a compound formed by the union of 2 mols. of diacetylhydrazobenzene and 1 mol. of azobenzene is obtained; this substance,  $N_2Ph_2 \cdot 2N_2Ph_2Ac_2$ , crystallises from acetic acid, alcohol, carbon disulphide, or light petroleum in large, orange prisms and melts at  $98.5-99^\circ$ . This product is not decomposed into its generators by repeated crystallisation, but when heated at  $190^\circ$  under reduced pressure the azobenzene distils off, leaving the diacetylhydrazobenzene unchanged. The compound is also produced by warming an alcoholic solution of its generators, but no analogous combination takes place when mixtures of azobenzene with hydrazobenzene, its monoacetyl derivative, or acetanilide are employed.

G. T. M.

**Formazyl Phenyl Ketone.** By EUGEN BAMBERGER and HUGO WITTER (*J. pr. Chem.*, 1902, [ii], 65, 139—149).—Details of the preparation of compounds previously described (Abstr., 1893, i, 157; 1894, i, 98).  
R. H. P.

**Action of Diazobenzene on Ethyl Acetoacetate, Acetoacetic Acid, and Ethyl Benzeneazoacetoacetate.** By EUGEN BAMBERGER and E. W. WHEELWRIGHT (*J. pr. Chem.*, 1902, [ii], 65, 123—138).—A detailed description of the preparation of compounds the formation of which has been previously described (Abstr., 1893, 84 and 156).  
R. H. P.

**Action of Sulphides, Sulphites, and Hydrosulphites on Nitrated Azo-colouring Matters.** By AUGUSTE ROSENSTIEHL and E. SUAIS (*Compt. rend.*, 1902, 134, 553—554. Compare Abstr., 1901, i, 429).—A nitrated azo-derivative is only attacked by an alkaline solution of calcium sulphide in such a way that the nitro-groups are converted into amino-groups, the calcium sulphide being oxidised to calcium thiosulphate. Sulphites, on the other hand, do not reduce the nitro-, but only the azo-group producing nitroanilines. *p*-Azoxyamines are attacked by sulphites, whilst the corresponding meta-derivatives are not touched. *p*-Azoxy-*o*-toluidine,



crystallises in brown needles melting at 188—189°. Hyposulphites easily reduce compounds which resist the action of sulphites; the nitrated azo-derivatives are converted into azoxyamino-derivatives; thus *m*-nitroazobenzene yields *m*-azoxyaniline (m. p. 150°).

K. J. P. O.

**Reduction of *o*-Nitroazo-colouring Matters; Production of Derivatives of 2-Phenyl- $\psi$ -aziminobenzene.** By AUGUSTE ROSENSTIEHL and E. SUAIS (*Compt. rend.*, 1902, 134, 606—608).—When the azo-colouring matters derived from *o*-nitroamines are treated in presence of an alkali with dextrose or an alkali sulphide, they yield quantitatively only one reduction product which is not affected by further treatment with the reducing agent. In this respect they differ markedly from the corresponding colouring matters derived from *m*- and *p*-nitroamines. The phenolazo-derivative from *o*-nitro-*p*-toluidine,  $\text{NO}_2\cdot\text{C}_7\text{H}_6\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , yields a colourless compound,  $\text{C}_{13}\text{H}_{11}\text{O}_2\text{N}_3$ , which melts at 240—241°, and forms a methyl derivative melting at 162—163°, and insoluble in alkali hydroxide solutions. When this product is treated with zinc and sodium hydroxide, it yields a crystalline compound which melts at 217—218°, and forms a methyl derivative melting at 102—103°. In this series of changes, the compound  $\text{NO}_2\cdot\text{C}_7\text{H}_6\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  is converted into the compound  $\text{C}_7\text{H}_6\langle\text{N}\rangle\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , and the latter into hydroxyphenyl- $\psi$ -*o*-aziminotoluene,  $\text{C}_7\text{H}_6\langle\text{N}\rangle\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ .  
C. H. B.

**Action of Acylcyanoacetic Esters on Diazonium and Tetrazonium Chlorides.** By G. FAVREL (*Bull. Soc. Chim.*, 1902, [iii], 27, 200—204).—The author has studied the action of benzene di-



azonium chloride and of diphenyltetra-azonium chloride on ethyl acetylcyanoacetate, ethyl propionylcyanoacetate, ethyl isobutyrylcyanoacetate, and ethyl benzoylcyanoacetate, and finds that, in general, diazonium and tetra-azonium chlorides act on the acyleyanoacetic esters with elimination of the acyl group and formation of the same substances as are produced by the action of diazonium and tetra-azonium chlorides on cyanoacetic esters.

A. F.

**Presence of Diazoamino- or Diazo-oxy-compounds in Azo-dyes.** By WILHELM VAUBEL (*Chem. Centr.*, 1902, i, 464; from *Zeit. Farben.-Textilchem.*, 1902, 1, 3—4).—The presence of diazoamino- or diazo-oxy-compounds has been detected in the following dyes by boiling with concentrated hydrochloric acid:—Sodium aminoazo-xylenesulphonate and the dyes obtained from diazotised naphthionic acid and  $\beta$ -naphthol- $\gamma$ -disulphonic acid,  $\alpha$ -diazonaphthalene and  $\beta$ -naphthol- $\gamma$ -disulphonic acid, diazotised naphthionic acid and naphthionate, diazonaphthalene-*o*-sulphonic acid and  $\alpha$ -naphthol-4-sulphonic acid, and *p*-diazobenzenesulphonic acid and  $\alpha$ -naphtholcarboxylic acid, all evolved nitrogen when thus treated. Nitrogen was not liberated in the following cases: aminoazobenzenesulphonic acid and the dyes prepared from diazotised naphthionic acid and  $\alpha$ -naphthol, diazotised naphthionic acid and  $\beta$ -naphthol,  $\beta$ -diazonaphthalene and gallic acid,  $\beta$ -diazonaphthalene-1-sulphonic acid and Neville and Winther's acid,  $\beta$ -diazonaphthalene-1-sulphonic acid and  $\beta$ -naphthol, diazotised sulphanilic acid and  $\beta$ -naphthol, diazotised sulphanilic acid and  $\beta$ -naphtholmonosulphonic acid, and tetrazodiphenyl and naphthionic acid.

E. W. W.

**Formation of Sugar from Proteids.** By OSCAR LOEW (*Beitr. chem. Physiol. Path.*, 1902, 1, 567—575).—A theoretical consideration of the subject in reference to the structure of the proteid molecule.

W. D. H.

**Production of Acetone from Crystallised Egg-albumin.** By ARNOLD ORGLER (*Beitr. chem. Physiol. Path.*, 1902, 1, 583).—When crystallised egg-albumin is treated with hydrogen peroxide and copper sulphate, acetone is one of the products obtained. Blumenthal and Neuberg (*Abstr.*, 1901, i, 433) show that the same is true for gelatin.

W. D. H.

**Fission of Albumin by Papayotin.** By OSKAR EMMERLING (*Ber.*, 1902, 35, 695—699).—Blood fibrin, when dissolved in a dilute alkaline solution containing toluene, and treated with papayotin from *Carica papaya* (Merck's preparation), undergoes digestion and yields large quantities of albumoses and peptones, together with smaller amounts of arginine, tyrosine, leucine, aspartic acid, glycine, glutamic acid, alanine, and phenylalanine. The tyrosine separates from the original mother liquor; the albumoses, peptones, and arginine are precipitated by means of phosphotungstic acid, whilst the amino-acids remaining in the filtrate are converted into their ethyl esters by treatment with ethyl alcohol and hydrogen chloride, these esters being subsequently separated by fractional distillation under reduced pressure (10 mm.).

This result indicates that papayotin behaves in a similar manner to trypsin. G. T. M.

**Fission of Albumin by Papayotin.** By OSKAR EMMERLING (*Ber.*, 1902, 35, 1012. Compare preceding abstract).—The hydrochloride of ethylglycine and not of ethyl glutamate is among the products formed. Phenylalanine is also probably present. J. J. S.

**Physiological and Acid Proteolysis.** By THOMAS BOKORNY (*Chem. Zeit.*, 1902, 26, 113—114).—Acid proteolysis takes place in the cold, although the action is slow. Five hundred grams of minced beef were allowed to stand for 22 months with 500 c.c. of 5 per cent. sulphuric acid; on heating to the boiling point, the whole mass liquefied, showing that the fibre had been converted into acid albumin. Treatment with zinc sulphate solution proved that albumoses were present in large quantity and the phosphomolybdate test indicated the presence of peptones. Other experiments also prove that treatment in the cold with dilute acid causes peptonisation of meat.

Purified egg-albumin, when boiled for 2 hours with 4 per cent. solutions of acids, is attacked to the greatest extent by hydrochloric acid, then follow hydrobromic acid, sulphuric acid, and oxalic acid in that order; acetic acid is almost inactive. This treatment resembles the peptic digestion of albumin, whilst the treatment with concentrated acid resembles the tryptic digestion.

The action of moulds (*Penicillium* and *Aspergillus*) on egg-albumin has been investigated. The proteolytic action takes place best when the solution contains 0.25 to 1 per cent. of acid: the optimum temperature is 35° to 40°.

Blood-albumin is most easily digested by moulds; casein, egg-albumin, and legumin are only digested to the extent of about 1 per cent. when left for 40 hours at 35° with a 1 per cent. sulphuric acid solution to which a mould has been added. J. McC.

**Abrin.** By WALTHER HAUSMANN (*Beitr. chem. Physiol. Path.*, 1902, 2, 134—142).—Abrin, which has been subjected to tryptic digestion and the proteids salted out, gives no biuret reaction; its poisonous characters remain unaltered, and it agglutinates red blood corpuscles as intensely as the unaltered abrin which contains proteids. Abrin, whether united to proteids or not, gives a precipitate with anti-abrin blood-serum. Abrin corresponds on the whole with ricin, but differs from it in that its agglutinating properties are resistant to pepsin—hydrochloric acid, even more resistant than its poisonous action. W. D. H.

**Albumoid of Bone.** By P. B. HAWK and WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1902, *Amer. J. Physiol.*, 6, xxvii—xxviii).—The collagenous residue, after extraction of the osseo-mucoid, when boiled in water yields an insoluble, elastin-like substance. It is more soluble in dilute acid and alkali than chondro-albumoid, and unlike the latter contains no loosely bound sulphur. It contains no phosphorus. Its percentage composition is, C, 50.03; H, 6.85; N, 15.93; S, 0.55; O, 26.64, which is very different from that of both elastin and keratin.

W. D. H.

**Reactions of Various Mucoids.** By L. D. MEAD and WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1902, *Amer. J. Physiol.*, **6**, xxviii).—Further experiments which show that the various connective tissue mucoids are practically identical. W. D. H.

**Soluble Compounds of Casein with Hydrogen Bromide or Iodide.** CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 124232).—*Casein hydrobromide*, a substance readily dissolving in warm water and containing 4 per cent. of bromine, is prepared by dissolving freshly precipitated casein in fuming hydrobromic acid; it is a white powder the solutions of which have a strongly acidic reaction. *Casein hydriodide* resembles the preceding compound, and is obtained in a similar manner. G. T. M.

**The Coagulation of Casein by Rennet and by Lactoserm.** By PAUL THEODOR MÜLLER (*Chem. Centr.*, 1902, i, 765—766; from *Münch. med. Woch.*, **49**, 372).—The power shown by the serum of animals which have been treated on Bordet's plan with milk proteids to precipitate caseinogen is dependent on the presence of calcium salts; barium salts will do instead, but magnesium and other salts are not effective. The specific serum, known as lactoserm, precipitates also boiled milk if a calcium salt is added. In the precipitation of caseinogen by means of lactoserm, no whey proteid is formed as in rennet coagulation. If the precipitate produced by lactoserm is dissolved by boiling with physiological salt solution, a precipitate is again produced by the addition either of lactoserm or rennet; in the latter case, whey proteid is also produced. The precipitability of the dissolved precipitate with ammonium sulphate is the same as that of fresh caseinogen; the conclusion is drawn that caseinogen is regenerated by boiling with physiological salt solution.

By strong acetic acid, a precipitate of the "precipitin" in an active condition is obtained from lactoserm. Lacto-precipitin is rendered inactive by prolonged heating at 70°, and acquires the property of inhibiting the precipitating action of fresh lactoserm. If the precipitin of lactoserm is removed by the addition of caseinogen, the residue has no such inhibiting characters; in this connection, calcium salts have no action. The inhibiting substance is precipitated by dilute acetic acid. After some hours, inactive lactoserm is able to dissolve the caseinogen precipitated by lactoserm; this property is not possessed by normal inactive rabbit's serum. Lactoserm, deprived of its precipitin by the addition of milk, acquires no inhibiting properties on subsequent heating to 75°; the inhibiting substance thus appears to be derived from the precipitin by the action of heat. Whilst normal inactive rabbit's serum has no anti-rennet action, inactive lactoserm inhibits the action of both rennet and fresh lactoserm. In the case of rennet curdling, excess of caseinogen neutralises the inhibiting effect. The inhibiting action is explained by the capacity of the inhibiting material to unite with caseinogen, and so shield it from the action of coagulating agents. The inhibiting substance, being a derivative of precipitin, is regarded as analogous to Eisenberg and Volk's "agglutinoids" and precipitoids, and in the

light of Ehrlich's theory this is compared to "receptors," the zymophore group of which is destroyed by heat, leaving the haptophore group untouched.

W. D. H.

**Elastin, Mucoïd, and other Substances in Elastic Tissue.** By A. N. RICHARDS and WILLIAM J. GIES (*Amer. J. Physiol.*, 1902, 7, 93—134).—Elastin has the following average percentage compositions: C, 54.14; H, 7.33; N, 16.87; S, 0.14; O, 21.52. No sulphur can be split off as sulphide by boiling with alkali. On decomposition with acid, only small proportions of nitrogen can be split off as ammonia and hexon bases, of which arginine, lysine, and histidine were identified. Elastin is not a 'fat proteid compound.' It digests readily in pepsin-hydrochloric acid; of the products, proto-elastose is most abundant, and the small amount of peptone points to resistance in the elastoses to progressive zymolysis. The combustion equivalent of elastin is 5925 calories. Elastic ligament contains mucoïd having the general properties of the other gluco-proteids of connective tissues. The proteids present coagulate at 50°, 65°, 75°, and 82°; these do not appear to arise wholly from adherent blood and lymph. There is also a small amount of nucleo-proteid; the composition of the gelatin obtained indicates that the collagen of elastic tissue is identical with that of bone and tendon. The combustion equivalent of the gelatin is 5276 cal. Among the crystalline extractives obtained from *ligamentum nuchæ* were creatine, hypoxanthine, and guanine.

W. D. H.

**Influence of Carbon Dioxide on the Action of Diastase.** By OTTO MOHR (*Ber.* 1902, 35, 1024—1029).—Maltose is not formed to any large extent by the action of diastase on starch when alkaline or neutral, although it is produced from acid samples of starch. In presence of carbon dioxide, however, about 30 per cent. of the starch is converted into maltose, whatever the nature of the sample of starch employed.

In presence of 0.01 gram of asparagine per 2.5 grams of starch, carbon dioxide further assists the formation of maltose, but hinders it if more than 0.05 gram of asparagine is present. Similarly, traces of lactic acid facilitate sugar-formation, but the action is less powerful if the quantity of acid is increased, or if carbon dioxide is also present.

T. M. L.

**A New Method of Observing Peptic Activity.** By E. I. SPRIGGS (*J. Physiol.*, 1902, 28; *Proc. Physiol. Soc.*, v—vi).—The viscosity of proteid solution in the presence of pepsin and 0.4 per cent. hydrochloric acid was estimated by an Ostwald's viscometer, and was found to fall rapidly. A fall also occurs, but more slowly, when the acid without the pepsin is present. As the viscosity falls the amount of coagulable proteid diminishes. Expressed in the form of a curve, the fall is first rapid, then slower, and finally insignificant; by this time, the coagulable proteid has nearly disappeared. A definite viscosity was found to correspond with a constant proportion between coagulable and non-coagulable proteid. The curves are capable of mathematical treatment, and there are indications that a simple ratio

exists between the amount of pepsin and the time required to produce a given amount of chemical change. W. D. H.

**Pepsin.** By CORNELIS A. PEKELHARING (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 412—423; *Zeit. physiol. Chem.*, 1902, 35, 8—30).—Slow precipitation of pepsin by ammonium sulphate causes it to separate out in the form of globulites; it was, however, not possible to obtain in this way a substance of constant composition. Better results may be obtained by dialysing dog's gastric juice (procured by Pawloff's method); when the percentage of hydrochloric acid sinks to 0.02 per cent., the pepsin is precipitated in the form of globulites. Six specimens of pepsin were prepared and analysed, and found to have a constant percentage composition. It is thus shown to be a proteid, and is free from phosphorus if care is taken to filter the gastric juice from its mucoid, nucleo-proteid; it, however, contains chlorine. Peptic activity is proportional to the amount of this proteid present, and is lost at the temperature at which the proteid is coagulated. It also exerts a rennet action on milk, causes the formation of plastein from albumose, but, unlike the original gastric juice, has no action on fats. On decomposition, it yields xanthine and a pentose; a proteid-like organic acid (*pepsinic acid*) is also described, having the composition C, 50.79; H, 7.02; N, 14.44; S, 1.08. W. D. H.

**Artificial Pepsin Digestions in the Presence of Alcohol.** By EUG. THIBAUT (*J. Pharm. Chim.*, 1902, [vi], 15, 5—13).—Alcohol and glycerol have a decided retarding influence on the digestive action of pepsin. In the case of the former, the lowest dilution at which any appreciable retarding influence is noticed is when the liquid contains about 4 per cent. of alcohol (90°), and in the latter, when the liquid contains 20 per cent. of glycerol. H. R. LE S.

**Chemical Nature of Tetanus Toxin.** By H. HAYASHI (*Chem. Centr.*, 1902, i, 272; from *Arch. exp. Path. Pharm.*, 1901, 47, 9—18).—The properties of the tetanus poison point to its being a proteid, probably a primary proteose. W. D. H.

**Aromatic Arsenic Compounds.** By AUGUST MICHAELIS (*Annalen*, 1902, 320, 271—344. Compare Abstr., 1883, 183, 327; 1885, 526; 1887, 367; 1892, 1321; 1894, i, 187).—Phenylchloroarsine,  $\text{AsPhCl}_2$ , when treated in ethereal solution with the sodium derivatives of alcohols and phenols, yields the corresponding esters of the hypothetical phenylarsenious acid,  $\text{AsPh}(\text{OH})_2$ .

[With P. FROMM].—*Dimethyl phenylarsenite*,  $\text{AsPh}(\text{OMe})_2$ , a colourless liquid with characteristic odour, boils at 116° under 18 mm. and at 220° under the ordinary pressure; it has a sp. gr. 1.343 at 20°. The ester is at once decomposed by water or alkaline solutions, yielding phenylarsenious oxide,  $\text{AsPhO}$ , and methyl alcohol; it forms a chlorine additive compound,  $\text{AsPh}(\text{OMe})_2\text{Cl}_2$ , which, on treatment with water, gives rise to phenylarsenic acid,  $\text{AsPhO}(\text{OH})_2$ , methyl alcohol, and hydrochloric acid.

*Diethyl phenylarsenite*,  $\text{AsPh}(\text{OEt})_2$ , boils at 122° under 15 mm. pressure and yields a chlorine additive compound,  $\text{AsPh}(\text{OEt})_2\text{Cl}_2$ .

*Diphenyl phenylarsenite*,  $\text{AsPh}(\text{OPh})_2$ , is an oily liquid boiling at  $245^\circ$  under 15 mm. pressure; it has a sp. gr. 1.32 at  $20^\circ$ ; under the action of chlorine, it gives rise to phenylarsenic tetrachloride,  $\text{AsPhCl}_4$ , and trichlorophenol. The corresponding *p*-tolyl ester boils at  $285^\circ$  under 12 mm. pressure and has a sp. gr. 1.2989 at  $13^\circ$ ; the *benzyl* ester is an oil having the odour of benzyl alcohol and boiling at  $296^\circ$  under 30 mm. pressure; it has a sp. gr. 1.2853 at  $13^\circ$ . *Di-β-naphthyl phenylarsenite*,  $\text{AsPh}(\text{O}\cdot\text{C}_{10}\text{H}_7)_2$ , crystallises in colourless needles melting at  $113$ — $114^\circ$ ; it resembles the preceding esters in being readily decomposed by water with the formation of phenylarsenious oxide.

*Catechol phenylarsenite*,  $\text{C}_6\text{H}_4\langle\text{O}\rangle\text{AsPh}$ , prepared by treating the lead derivative of catechol with a xylene solution of phenylchloroarsine, is a white, crystalline substance melting at  $83^\circ$  and boiling at  $197$ — $198^\circ$  under 15 mm. pressure. The interaction of phenylchloroarsine and the sodium derivative of catechol results in the formation of a substance still containing chlorine.

*Phenylarsenimide*,  $\text{AsPh}\cdot\text{NH}$ , produced by passing dry ammonia gas into a benzene solution of phenylchloroarsine, is a crystalline substance readily decomposed by moisture into phenylarsenious oxide and ammonia; it crystallises from alcohol in leaflets, sinters at  $265^\circ$ , and melts at  $270^\circ$ .

The esters of phenylarsenic acid are most readily obtained by the action of the alkyl iodides on *silver phenylarsenate*,  $\text{AsPhO}(\text{OAg})_2$ ; this salt, which is prepared from silver nitrate and a solution of neutral ammonium phenylarsenate, crystallises in nacreous plates.

*Dimethyl phenylarsenate*,  $\text{AsPhO}(\text{OMe})_2$ , is a colourless liquid with a disagreeable odour boiling at  $188^\circ$  under 95 mm. pressure; it has a sp. gr. 1.3946 at  $23^\circ$ . The corresponding *ethyl* ester boils at  $168$ — $170^\circ$  under 15 mm. pressure and has a sp. gr. 1.318 at  $15^\circ$ ; chlorine converts it into phenyloxychloroarsine, chloral, and hydrogen chloride. Both esters are decomposed by water yielding phenylarsenic acid and the corresponding alcohol.

[With V. BRUDER.]—Dimethylaminophenylarsenic acid,  
 $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OH})_2$ ,

prepared by treating dimethylaminophenylarsenious oxide with water and red mercuric oxide, crystallises in long, colourless needles which sublime without melting.

[With K. ULRICH.]—Phenyldiethylarsine,  $\text{AsPhEt}_2$ , combines with methyl iodide at the ordinary temperature to form *phenylmethyldiethylarsonium iodide*,  $\text{AsPhEt}_2\text{MeI}$ , which crystallises in prisms melting at  $122^\circ$ .

*Phenyltriethylarsonium iodochloride*,  $\text{AsPhEt}_3\cdot\text{ICl}_2$ , produced by passing chlorine into an acetic acid solution of the quaternary iodide, separates in dark yellow crystals.

*Phenyliodomethyldiethylarsonium iodide*,  $\text{AsEt}_2\text{PhI}\cdot\text{CH}_2\text{I}$ , produced by heating phenyldiethylarsine with methylene iodide on the water-bath, crystallises from dilute alcohol in needles and melts at  $173^\circ$ .

*Phenyldiethylarsenobetaine chloride*,  $\text{AsPhEt}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , obtained by warming a mixture of phenyldiethylarsine and chloroacetic acid,

crystallises from ether and alcohol in white needles and melts at  $135^{\circ}$ ; it is readily soluble in water. The *platinichloride* forms lustrous, red crystals melting at  $161^{\circ}$ . The betaine is set free by the action of alcoholic potassium hydroxide; the corresponding *ethyl ester*,  $\text{AsPhEt}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , obtained by heating the arsine with ethyl chloroacetate at  $100^{\circ}$ , crystallises in needles and melts at  $125^{\circ}$ ; its crystalline picrate melts at  $90^{\circ}$ .

When pure, anisylchloroarsine melts at  $48^{\circ}$  and boils at  $160^{\circ}$  under 30 mm. pressure. Anisylarsenic acid (m. p.  $203^{\circ}$ ), when heated with phosphorus acid, yields *arsenoanisole*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{As}\cdot\text{As}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , this substance being a yellow, amorphous powder decomposing at  $200^{\circ}$ .

[With H. HILBENZ.]—*Phenetylchloroarsine*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{AsCl}_2$ , produced by heating triphenetylarsine with arsenious chloride at  $220^{\circ}$ , is a colourless liquid boiling at  $198^{\circ}$  under 28 mm. pressure; dry chlorine converts it into a solid *tetrachloride*, *phenetylarsenic acid*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OH})_2$  (m. p.  $209\text{--}210^{\circ}$ ), being formed in the presence of water; sodium carbonate yields the *oxide*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}$ . *Arsenophenetole*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{As}\cdot\text{As}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$ , is a yellow powder which readily becomes resinous.

[With K. ULRICH and F. ZIEGLER.]—*p*-Tolylchloroarsine crystallises in colourless, refractive plates melting at  $31^{\circ}$  and boiling at  $267^{\circ}$  under the ordinary pressure. *Arseno-p-toluene*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{As}\cdot\text{As}\cdot\text{C}_6\text{H}_4\text{Me}$ , obtained by the action of phosphorous acid on *p*-tolylarsenious oxide, crystallises from chloroform in lustrous needles and melts at  $184^{\circ}$ ; chlorine converts it successively into di- and tetra-chlorides, nitric acid oxidises it to *p*-tolylarsenic acid.

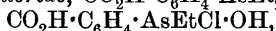
*p*-Tolylarsenious sulphide,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{AsS}$ , produced by passing hydrogen sulphide into an alcoholic solution of the corresponding oxide, separates from benzene in white, lustrous crystals and melts at  $146^{\circ}$ .

*p*-Tolylarsenic sesquisulphide,  $\begin{matrix} \text{C}_6\text{H}_4\text{Me}\cdot\text{As}\cdot\text{S} \\ \text{C}_6\text{H}_4\text{Me}\cdot\text{As}\cdot\text{S} \end{matrix} \rangle \text{S}$ , resulting from the

action of hydrochloric acid on an ammoniacal solution of *p*-tolylarsenic acid saturated with hydrogen sulphide, is separated from the sulphur simultaneously set free by solution in benzene; it crystallises from this solvent in white needles and melts at  $119\text{--}120^{\circ}$ .

[With H. KLATT.]—*p*-Tolyl dimethylarsine,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{AsMe}_2$ , prepared by treating the chloroarsine with excess of zinc methyl in ethereal solution, is a colourless liquid having a disagreeable odour and boiling undecomposed at  $220^{\circ}$  in an atmosphere of carbon dioxide; the *quaternary iodide*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{AsMe}_3\text{I}$ , crystallises from water in plates which dissociate on heating; the *platinichloride*,  $(\text{C}_6\text{H}_4\text{Me}\cdot\text{AsMe}_3)_2\text{PtCl}_6$ , forms reddish-yellow leaflets and melts at  $225^{\circ}$ . *Tolyl-p-diethylarsine* is a colourless, refractive liquid boiling at  $250^{\circ}$ ; its *methiodide*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NEt}_2\cdot\text{MeI}$ , crystallises in colourless leaflets and melts at  $220^{\circ}$ ; the *ethiodide* is crystalline, has a bitter taste, and melts at  $230^{\circ}$ ; the *platinichloride* forms reddish-yellow leaflets melting at  $210^{\circ}$ .

[With EPPENSTEIN.]—*p*-Oxydiethylarsinibenzoic acid is obtained in the form of its *hydrochloride*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{AsEt}_2\text{O}\cdot\text{HCl}$  or



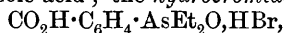
by oxidising diethyl-*p*-tolylarsine with an aqueous solution of potassium

permanganate, saturating the filtrate with hydrogen chloride, evaporating to dryness, and crystallising the residue from alcohol; the salt forms white crystals melting at  $162^{\circ}$ , and yields the *mercurichloride*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{AsEt}_2\text{O}, \text{HCl}, \text{HgCl}_2$ , a white substance melting at  $182^{\circ}$ .

*p*-Thiodiethylarsinobenzoic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{AsEt}_2\text{S}$ , produced by the action of hydrogen sulphide on an aqueous solution of the preceding compound, crystallises from water in long, colourless needles and melts at  $184^{\circ}$ .

*p*-Diethylarsinobenzoic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{AsEt}_2$ , obtained by reducing the preceding oxy-acid with tin and hydrochloric acid, crystallises in white needles and melts at  $58^{\circ}$ ; it forms additive compounds with sulphur and methyl iodide, its *metallic* salts, excepting those of the alkali metals, are insoluble; its *mercurichloride*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{AsEt}_2, \text{HgCl}_2$ , crystallises in white, silky leaflets and melts at  $171\text{--}172^{\circ}$ .

The halogens form additive products with this acid, which readily absorb moisture, giving rise to the corresponding halogen salt of *p*-oxydiethylarsinobenzoic acid; the *hydrobromide*,



melts at  $144\text{--}145^{\circ}$ , and the hydriodide at  $84^{\circ}$ . The *methiodide* of *p*-diethylarsinobenzoic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{AsEt}_2, \text{MeI}$ , forms white needles melting at  $131^{\circ}$ .

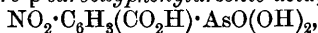
*p*-Triethylarsenibenzobetaine,  $\text{C}_6\text{H}_4\langle\text{AsEt}_3\rangle\text{O}$ , prepared by oxidising

*p*-tolyltriethylarsonium chloride with alkaline permanganate solution, forms a hygroscopic *hydrochloride* from which it is obtained by alkalis; it crystallises in hygroscopic plates having a bitter taste and does not form salts with alkali hydroxides; it is completely decomposed by alcoholic potassium hydroxide, yielding triethylarsenious oxide and potassium benzoate. The *platinichloride*,  $(\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{AsEt}_3)_2\text{PtCl}_6$ , forms pale yellow leaflets melting at  $225^{\circ}$ ; the *aurichloride* crystallises in golden-yellow needles and melts at  $165^{\circ}$ ; the *picrate* separates in yellow leaflets melting at  $155^{\circ}$ .

*p*-Trimethylarsenibenzobetaine,  $\text{C}_6\text{H}_4\langle\text{AsMe}_3\rangle\text{O}$ , crystallises in

leaflets, with  $2\frac{1}{2}\text{H}_2\text{O}$ ; the *hydrochloride* and *hydrobromide* separate from water in white needles decomposing respectively at  $400^{\circ}$  and  $270^{\circ}$ ; the *platinichloride* and *aurichloride* form yellow needles melting respectively at  $255^{\circ}$  and  $198^{\circ}$ ; the *nitrate* is obtained in leaflets melting at  $230^{\circ}$ .

*Nitro-p-tolylarsenic acid*,  $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{AsO}(\text{OH})_2$ , prepared from *p*-tolylarsenic acid by the action of nitrosulphuric acid, crystallises in rhombic prisms and does not melt below  $300^{\circ}$ ; the alkali and *silver* salts are amorphous; the *acid barium* salt,  $[\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{As}(\text{OH})\cdot\text{O}]_2\text{Ba}$ , separates from its aqueous solution in white needles; the *calcium* salt forms lustrous leaflets. The salts retain  $1\text{H}_2\text{O}$  very tenaciously even at  $180^{\circ}$ . *Amino-p-tolylthioarsenic acid*,  $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{AsS}(\text{SH})_2$ , obtained by reducing the preceding acid with ammonium sulphide, is isolated in the form of its *sulphate*, a yellow, amorphous powder decomposing at  $155^{\circ}$ . *Nitro-p-carboxyphenylarsenic acid*,





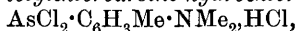
produced by oxidising nitro-*p*-tolylarsenic acid with alkaline permanganate, crystallises in white needles soluble in water or alcohol; it does not melt below 300°.

*Dinitroarseno-p-toluene*,  $\text{As}_2(\text{C}_6\text{H}_3\text{Me}\cdot\text{NO}_2)_2$ , formed by the action of phosphorous acid on nitro-*p*-tolylarsenic acid, is a yellow substance melting at 165°; when treated with bromine, it yields nitro-*p*-tolylbromoarsine,  $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{AsBr}_2$ , which separates from chloroform in light brown, lustrous scales decomposing at 260°.

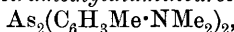
*Nitro-p-tolylarsenious sulphide*,  $\text{NO}_2\cdot\text{C}_5\text{H}_3\text{Me}\cdot\text{AsS}$ , produced on passing hydrogen sulphide into an aqueous solution of nitro-*p*-tolylarsenic acid, is separated from the sulphur deposited by dissolving in ammonia solution or in benzene; it is obtained in yellow needles melting at 141—142°.

*o-Dimethylamino-p-tolylarsenious oxide*,  $\text{NMe}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{AsO}$ , prepared by heating a mixture of arsenious chloride and dimethyl-*o*-toluidine, is a white, amorphous powder melting at 55°.

*o-Dimethylamino-p-tolylchloroarsine hydrochloride*,



resulting from the action of concentrated hydrochloric acid on the preceding oxide, crystallises in needles having a pungent odour and melting at 145°; the *hydrobromide* is obtained in rhombic plates melting at 168°; the *hydriodide* is a red, crystalline powder; the *sulphide*,  $\text{S}\cdot\text{NMe}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{AsS}$ , formed by passing hydrogen sulphide into an alcoholic solution of the oxide, separates as a pale yellow powder and melts at 65—67°. *oo-Tetramethyldiaminoarseno-p-toluene*,



prepared from the oxide and phosphorous acid in alcoholic solution, is a pale yellow powder melting at 75°.

*o-Dimethylamino-p-tolylarsenic acid*,  $\text{NMe}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{AsO}(\text{OH})_2$ , obtained from the oxide by the action of water and red mercuric oxide, forms grey leaflets and melts at 245°.

[With HERMANN EISENLOHR.]—*m-Tolylchloroarsine* is a refractive oil boiling at 270°; the *tetrachloride*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{AsCl}_4$ , melts at 38°; the *oxide*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{AsO}$ , obtained by treating the chloroarsine with sodium carbonate, is a fibrous, viscid mass, which yields *m-arsenotoluene*, (m. p. 106°) on treatment with phosphorous acid.

*m-Tolylarsenic acid*, produced from the tetrachloride, crystallises in needles and melts at 150°; when heated at 220—230°, it yields the *anhydride*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{AsO}_2$ ; its *ammonium hydrogen*, *phenylhydrazine hydrogen*, *calcium*, and other *metallic salts* are described.

*m-Carboxyphenylarsenic acid*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OH})_2$ , obtained by oxidising the preceding acid, crystallises in lustrous leaflets and yields the *anhydride*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_2$ , on heating; its *calcium salt*,

$\text{C}_6\text{H}_4\begin{array}{c} \text{CO} \text{---} \text{O} \\ \diagup \quad \diagdown \\ \text{AsO}(\text{OH})\text{O} \end{array} \text{Ca}$ , crystallises in four-sided-plates; the *silver salt*,  $\text{CO}_2\text{Ag}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OAg})_2$ , is a white precipitate.

[With R. SEEMANN.]—*m-Xylylchloroarsine* crystallises in colourless needles melting at 42—43°; the *tetrachloride*,  $\text{C}_8\text{H}_9\text{AsCl}_4$ , is a white, crystalline mass yielding the *oxychloride*,  $\text{C}_8\text{H}_9\text{Me}_2\cdot\text{AsOCl}_2$  (m. p. 150°), and the *acid*,  $\text{C}_8\text{H}_9\text{Me}_2\cdot\text{AsO}(\text{OH})_2$ , on treatment with water. *m-Xylyl-*

*arsenious oxide*,  $C_6H_5Me_2 \cdot AsO$ , melts at  $220^\circ$ , and the *sulphide*,  $C_6H_5Me_2 \cdot AsS$ , crystallises in white needles melting at  $169^\circ$ . *Arseno-m-xylene* crystallises from chloroform in lustrous, white needles and melts at  $194-196^\circ$ ; the additive product, *iodoarseno-m-xylene*,  $C_6H_5Me_2 \cdot AsI \cdot AsI \cdot C_6H_5Me_2$ , melts at  $89^\circ$ . *m-Xylylarsenic acid* is also obtained by oxidising the chloroarsine or the corresponding oxide; it forms quadratic crystals and melts at  $210^\circ$ ; its *ammonium* salt melts at  $136^\circ$ . *Monochloro-m-xylylarsenic acid*,  $C_6H_4Me_2Cl \cdot AsO(OH)_2$ , results from the oxidation of the chloroarsine or the preceding compound with chlorine in aqueous solution; it crystallises in needles and melts at  $165^\circ$ ; *dichloro-m-xylylarsenic acid*,  $C_6H_4Me_2Cl_2 \cdot AsO(OH)_2$ , formed by oxidation with chlorine in glacial acetic acid, melts at  $193^\circ$ . *Nitro-m-xylylarsenic acid* crystallises in white needles melting at  $207^\circ$ . *m-Carboxytolylarsenic acid*,  $CO_2H \cdot C_6H_3Me \cdot AsO(OH)_2$ , obtained from the xylyl acid with permanganate solution, does not melt below  $300^\circ$ ; *dicarboxyphenylarsenic acid*,  $C_6H_3(CO_2H)_2 \cdot AsO(OH)_2$ , is produced when a double quantity of oxidising agent is employed.

[With PASEL].—*p-Xylylchloroarsine* is obtained in needles melting at  $285^\circ$ ; the *oxide* melts at  $165^\circ$  and yields the *iodoarsine*,  $C_8H_9AsI_2$  (m. p.  $45^\circ$ ), with concentrated hydriodic acid and the *oxychloroarsine* with chlorine, the latter derivative melting at  $178^\circ$ . *Arseno-p-xylene* melts at  $208^\circ$  and its *di-iodide* at  $97^\circ$ . *p-Xylylarsenious sulphide*  $C_8H_9AsS$ , melts at  $188^\circ$  and the *disulphide* at  $95^\circ$ . *p-Xylylarsenic acid* crystallises in needles melting at  $223^\circ$ ; its *nitro*-derivative forms pale yellow needles, melts at  $205^\circ$ , and when treated with phosphorous acid yields *arsenonitro-p-xylene*, a yellow powder sintering at  $165^\circ$ . *p-Carboxytolylarsenic acid* melts at  $208^\circ$ .

[With W. OBERG].— $\psi$ -*Cumylchloroarsine* and  $\psi$ -*cumylarsenic acid*,  $C_9H_{11}AsO(OH)_2$ , crystallise in white needles melting respectively at  $82.5^\circ$  and  $224^\circ$ .

*p-Cumylchloroarsine* is an oil boiling at  $170^\circ$  under 30 mm. pressure; *p-cumylarsenic acid* crystallises in lustrous, white needles, melts at  $152^\circ$ , and when oxidised by permanganate gives rise to *p-carboxyphenylarsenic acid*.

[With A. TRÄGEL].—*tert. Butylphenylchloroarsine*,  $CMe_3 \cdot C_6H_4 \cdot AsCl_2$ , a colourless oil boiling at  $175-180^\circ$  under 20 mm. pressure, yields an *oxide* melting at  $89^\circ$ , a *sulphide* melting at  $292^\circ$ , and *arsenotert. butylbenzene* melting at  $198^\circ$ ; the *acid*,  $CMe_3 \cdot C_6H_4 \cdot AsO(OH)_2$ , crystallises in needles and melts at  $193^\circ$ .

[With E. BÜSCHLER].— $\beta$ -*Naphthylchloroarsine*,  $C_{10}H_7 \cdot AsCl_2$ , prepared from mercury- $\beta$ -dinaphthyl, and arsenious chloride, crystallises from light petroleum in aggregates of needles melting at  $69^\circ$ ; the *oxide* is amorphous and melts at  $270^\circ$ ; *arseno- $\beta$ -naphthalene*,  $As_2(C_{10}H_7)_2$ , crystallises from xylene in needles and melts at  $234^\circ$ .  $\beta$ -*Naphthylarsenic acid* crystallises from water in needles and melts at  $155^\circ$ . G. T. M.

## Organic Chemistry.

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**Action of Nitrosulphuric Acid on Saturated Hydrocarbons.** By WLADIMIR MARKOWNIKOFF (*Ber.*, 1902, 35, 1584—1587).—The author maintains, in spite of recent statements to the contrary (Zaloziecki and Frasch, *Ber.*, 1902, 35, 386), that at the ordinary temperature nitrosulphuric acid is without action on the paraffins and polymethylenes, and that in many cases the temperature can be raised considerably without action occurring. Thus diisopropyl and methylpentamethylene can be distilled from the acid mixture without being changed, and dihexanaphthene, diheptanaphthene, dimenthyl, ethylnaphthene, propylnaphthene, ethylmenthane, and pure disuberyl are not affected at the ordinary temperature. When disuberyl is contaminated with suberylene or its polymerides, however, it is vigorously attacked, being partly nitrated, partly oxidised. Methylcyclohexane is only slowly acted on at 75—80°.

The author criticises the statement that dinitrobenzene and its homologues were not obtained by Zaloziecki and Frasch on nitrating the fraction of Galician petroleum boiling at 59—65°; he has often isolated dinitrobenzene from naphtha distillates of low boiling point.

W. A. D.

**The Addition of Hypochlorous Acid to Propylene.** By LOUIS HENRY (*Compt. rend.*, 1902, 134, 1070—1072).—A reply to Tiffeneau (*Compt. rend.*, 1902, 134, 774). The author believes that the two chlorohydrins,  $\text{CH}_2\text{Cl}\cdot\text{CHMe}\cdot\text{OH}$  and  $\text{OH}\cdot\text{CH}_2\cdot\text{CHMeCl}$ , are produced by the action of hypochlorous acid on propylene. By the action of hypochlorous acid on allylene derivatives, the hydroxyl group is, for the main part, attached to the  $\text{:CH}_2$  group.

J. MCC.

**Aliphatic Nitro-compounds.** By HEINRICH BILTZ (*Ber.*, 1902, 35, 1528—1533).—When tetrachloroethylene is heated with nitrogen peroxide under pressure, a quantitative yield of tetrachlorodinitroethane is obtained (compare Kolbe, *Ber.*, 1869, 2, 326, and Hoch, this Journal, 1873, 364); it melts and decomposes at 143—144°. *Tetrabromodinitroethane*, obtained in an analogous manner from tetrabromoethylene, crystallises from light petroleum, is soluble in alcohol or benzene, and melts and decomposes at 154—156°.

*Diphenyldichlorodinitroethane*, obtained when diphenyldichloroethylene is heated in a sealed tube with nitrogen peroxide for 3—4 hours at 50—60°, is a yellow, viscous oil with an odour like chloropierin.

$\alpha$ -Dichlorostyrene and  $\alpha\alpha\beta$ -trichlorostyrene do not form additive compounds with nitrogen peroxide.

R. H. P.

**Oxidation of Tetrachloro- and Tetrabromo-ethylene.** By HEINRICH BILTZ (*Ber.*, 1902, 35, 1533—1537).—It is shown that when tetrachloro- and tetrabromo-ethylene are treated with a mixture of sulphuric and nitric acids according to Hoch's method (this Journal, 1873, 364), they are oxidised and converted into trichloroacetyl chloride and tribromoacetyl bromide respectively.

*Tribromoacetyl bromide* is a colourless oil which only reacts slowly with water. R. H. P.

**Separation of the Amyl Alcohols from Fusel Oil. III.** By WILHELM MARCKWALD (*Ber.*, 1902, 35, 1595—1601. Compare Abstr., 1901, i, 248).—The amyl alcohol obtained from molasses spirit contains a much larger proportion (48—58 per cent.) of the active alcohol than that prepared from grain or potato spirit (13·5—22 per cent.). Details are given for separating pure inactive amyl alcohol from fusel oil by fractionally crystallising the derived mixture of barium amyl sulphates; these salts crystallise together in an unbroken series of mixed crystals, and, by careful procedure, 200 grams of pure barium isoamyl sulphate can be obtained from 700 grams of the mixed salts. The active salt can be isolated, but with somewhat greater difficulty from the more soluble fractions.

The solubility of barium isoamyl sulphate in 100 parts of water is 11·85 at 19·3° and 12·15 at 20·5°; that of the corresponding active amyl salt,  $(C_5H_{11}O_4S)_2Ba, 2H_2O$ , is 26·10 at 20·5°,  $[\alpha]_D$  varying from +2·58 to +2·71 for concentrations ranging from  $c=20$  to  $c=4$ . As the specific rotatory power of the salt is not affected by the presence of barium isoamyl sulphate, the composition of mixtures of the two salts can be determined from their optical activity. W. A. D.

**Preparation of Acetic Anhydride.** FARBENFABRIKEN VORM. F. BAYER & Co. (D. R. P. 127350).—Acetic anhydride is readily prepared by treating dry sodium acetate at 20° with a mixture of chlorine and sulphur dioxide in approximately molecular proportion, the latter gas being slightly in excess. The gases are rapidly absorbed, and a semi-crystalline magma is formed from which the acetic anhydride is distilled. G. T. M.

**Beryllium Compounds of the Type  $Be_4O(OR)_6$ .** By H. LACOMBE (*Compt. rend.*, 1902, 134, 772—774).—The action of acids of the acetic series on beryllium carbonate yields compounds of the type  $Be_4O(OR)_6$ , in which R is the acid radicle. The lower members are crystalline solids and the higher members are liquid; all of them volatilise without decomposing under ordinary or reduced pressure:

	Melting point.	Boiling point normal pressure.	Boiling point under 19 mm. pressure.
Beryllium formate .....	{ sublimes without melting	—	—
„ acetate .....	283—284°	330—331°	{ sublimes without melting
„ propionate ...	119—120	339—341	221°
„ isobutyrate...	76	336—337	216
„ butyrate .....	liquid	—	239
„ isovalerate...	liquid	—	254

They are all insoluble in cold water, but are dissolved and decomposed by boiling water. The formate is insoluble in all organic solvents; the acetate is soluble only in chloroform, whilst the others

are soluble in all ordinary solvents. In benzene, the molecular weights determined cryoscopically are lower than the calculated numbers, whilst in ethylene bromide they are higher than, but approximate fairly closely to, the calculated numbers.

The author was unable to obtain normal beryllium salts of the acids of the acetic series, and on the other hand could not obtain inorganic salts of this special type.

C. H. B.

The Fatty Oil contained in the Seeds of *Lindera Benzoin*. II. **Lauric Acid and some of its Derivatives.** By CHARLES E. CASPARI (*Amer. Chem. J.*, 1902, 27, 291—311).—These seeds yield by extraction with ether 58.1 per cent., and by expression 34.5 per cent. of a yellow fat melting at 26° and soluble in alcohol, benzene, light petroleum, or acetone. The saponification number is 284.8, and the Reichert number 1.29 to 1.34. The fat consists of a mixture of the glycerides of decoic (capric), lauric, and oleic acids. The author records melting and boiling points for lauric acid and its amide and chloride differing slightly from those previously recorded by Krafft; the *anilide* forms fluffy needles melting at 76.5°, and the *o-toluidide* white needles melting at 81.5°; the barium, *strontium*, *magnesium hydrogen*, lead, manganese, zinc, and cobalt salts of lauric acid have also been prepared and their composition determined (compare Oudemans, *J. pr. Chem.*, 1863, 89, 331).

T. A. H.

**Constitution of Campholenic and Nitro-campholenic Acids.** By AUGUSTE BEHAL (*Bull. Soc. Chim.*, 1902, [iii], 27, 402—412).—By treating the lactone of  $\beta$ -campholenic acid with bromine, *bromocampholenolactone*,  $\text{CH}_2 \begin{array}{c} \text{CMe}_2 \cdot \text{CMe} \cdot \text{O} \\ \text{CH}_2 - \text{CBr} \cdot \text{CH}_2 \end{array} \text{CO}$ , is obtained as a crystalline substance which has the odour of camphor and melts at 146°.

It is very soluble in alcohol and in benzene, and soluble in twice its weight of light petroleum. When heated with aqueous or alcoholic sodium hydroxide, it yields a salt of dihydroketocampholenic acid; if alkali carbonate is employed, the lactone of the dihydroketocampholenic acid (dehydrocampholenolactone),  $\text{CH}_2 \begin{array}{c} \text{CMe}_2 \cdot \text{CMe} \cdot \text{O} \\ \text{CH}_2 - \text{C} = \text{CH} \end{array} \text{CO}$ , which melts

at 32° and boils at 193° under 19 mm. pressure, is obtained. This is unsaturated, and with bromine forms a dibromo-compound which melts at 99—100°; it is oxidised by permanganate with formation of

dihydroxycampholenolactone,  $\text{CH}_2 \begin{array}{c} \text{CMe}_2 \cdot \text{CMe} \cdot \text{O} \\ \text{CH}_2 - \text{C}(\text{OH}) \cdot \text{CH}(\text{OH}) \end{array} \text{CO}$ , melt-

ing at 128°. The acid corresponding with the dihydroxylactone has not been obtained. The lactone in turn undergoes oxidation with formation of oxalic, dimethylhexanonic, and dimethylævulic acids, a result which is not in accord with the formula for dehydrocampholenolactone put forward by Tiemann (*Abstr.*, 1897, i, 249). When heated under the ordinary pressure, dehydrocampholenolactone gives off carbon dioxide and an almost quantitative yield is obtained of a hydrocarbon, *didehydrocampholene*,  $\text{C}_9\text{H}_{14}$ , which boils at 127—128° under 757 mm. pressure.

When dehydrocampholenolactone is heated in a sealed tube with alcoholic ammonia, an *amide* is formed which melts at 236°. *Methyl ketocampholenate*, obtained by heating sodium ketocampholenate with methyl iodide in alcoholic solution, is a liquid which boils at 135–138° under 33 mm. pressure and has a sp. gr. 1.068 at 0°. *Ethyl keto-*

*campholenate*,  $\text{CH}_2 \begin{array}{l} \diagup \text{CMe}_2 \cdot \text{CMe} \\ \diagdown \text{CH}_2 - \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \end{array} \text{CH}_2 \cdot \text{CO}_2\text{Et} \end{array}$ , boils at 147–148° under 25 mm.

pressure; *benzyl ketocampholenate* is a crystalline substance which melts at 46–47°.

The author considers that Tiemann's view that dihydroketocampholenic acid contains an ethylene oxide group should be accepted. As a consequence of the formula which the author proposes, it would follow that a tertiary alcoholic group in the  $\gamma$ -position relatively to a carboxyl group and having an adjoining ethylene bond has a tendency to pass into a saturated compound having an ethylene oxide grouping.

A nomenclature for the campholanes and campholenic acids and their derivatives is proposed.

A. F.

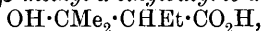
**Pulegenic Acid.** By LOUIS BOUYEAULT and LÉON TÉTRY (*Bull. Soc. Chim.*, 1902, [iii], 27, 307–313).—In preparing pulegenic acid by Wallach's method (Abstr., 1896, i, 309), the authors have isolated two compounds not observed by the former investigator. The first of these is a *lactone*, isomeric with pulegenic acid, which crystallises in small, transparent prisms melting at 79–80°; it is insoluble in water or sodium carbonate, but readily soluble in alkali hydroxides and in organic solvents. This lactone is formed only in very small quantities but is different from the lactone obtained by Wallach, which can be obtained by boiling pulegenic acid with dilute sulphuric acid. Another isomeride of pulegenic acid is also produced in the reaction; this is a colourless oil with neutral reaction, which boils at 113° under 21 mm. pressure, combines with bromine, and contains neither a hydroxyl nor a carbonyl group.

The authors have also prepared the *anilide* and the *p-toluidide* of pulegenic acid. The former, obtained by heating pulegenic acid with aniline for several hours at a temperature of 190–200°, crystallises from light petroleum in colourless needles melting at 123°; it is very soluble in alcohol or in ether, sparingly so in light petroleum, and is attacked by alcoholic potassium hydroxide only when heated with it in a sealed tube at above 180°. The *p-toluidide*, obtained in a similar manner to the anilide, forms slender, colourless needles which melt at 143°, is very soluble in ether, but sparingly so in light petroleum.

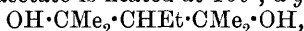
A. F.

**Action of Organomagnesium Compounds on  $\beta$ -Ketonic Esters.** By VICTOR GRIGNARD (*Compt. rend.*, 1902, 134, 849–851. Compare Abstr., 1901, i, 250, 263, 393, 679, and this vol., i, 198).—In addition to small quantities of methane and hydrogen, ethyl acetoacetate and magnesium methiodide yield products from which water regenerates the unchanged ester and magnesium iodide; the ester reacts in its enolic form. From ethyl ethylacetoacetate and magnesium methiodide, the unchanged ester, and an ester,  $\text{OH} \cdot \text{CMe}_2 \cdot \text{CHEt} \cdot \text{CO}_2\text{Et}$ , are

obtained; on hydrolysis with 10 per cent. potassium hydroxide, the latter yields  $\beta$ -hydroxy- $\beta$ -methyl- $\alpha$ -ethylbutyric acid,



which crystallises in needles melting at  $71-72^\circ$ , and boils at  $147^\circ$  under 10 mm. pressure. If the mixture of magnesium methiodide and ethyl ethylacetoacetate is heated at  $100^\circ$ , a *glycol*,



is obtained together with unchanged ester; the former crystallises in slender needles melting at  $52^\circ$  and boils at  $127-128^\circ$  under 11 mm. pressure.

Methyl diethylacetoacetate and magnesium methiodide react at the ordinary temperature, producing methyl  $\alpha$ -ethylbutyrate (b. p.  $135-137^\circ$  under 736 mm. pressure); when the two substances are heated together at  $100^\circ$  under pressure, a small quantity of an unsaturated hydrocarbon,  $\text{C}_5\text{H}_{16}$ , is obtained; it boils at  $115-120^\circ$  under 750 mm. pressure, and probably is formed by the dehydration of an alcohol,  $\text{CHEt}_2 \cdot \text{CMe}_2 \cdot \text{OH}$ .

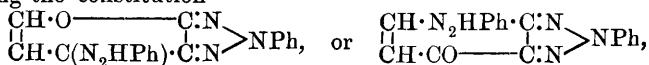
Ethyl ethylideneacetoacetate and magnesium methiodide yield a liquid which decomposes on hydrolysis with the formation of methyl isobutyl ketone (b. p.  $113-116^\circ$  under 753 mm. pressure). From this result it would appear that ethyl ethylideneacetoacetate is represented

by Claisen's formula,  $\text{O} \begin{array}{c} \text{CMe} \\ \diagup \quad \diagdown \\ \text{CHMe} \end{array} \text{C} \cdot \text{CO}_2\text{Et}.$

K. J. P. O.

**Tautomerism of Pyromeconic Acid.** By ALBERTO PERATONER (*Atti R. Accad. Lincei*, 1902, [v], 11, i, 246—250).—It has been shown by the author and Leonardi (Abstr., 1900, i, 550) that pyromeconic acid exhibits reactions indicating both an enolic and a ketonic structure. The author now finds that the nitrosodipyromeconic acid obtained by Ost (Abstr., 1879, 708) by the interaction of nitrous and pyromeconic acids is derived from the ketonic modification, and is really an *isonitroso*-derivative having the constitution  $\text{CH} \begin{array}{c} \text{CH}-\text{O} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{CO} \end{array} \text{C} \cdot \text{NOH}, \text{C}_5\text{H}_4\text{O}_3.$

A better method than that of Ost for preparing this compound is by the action of an alkyl nitrite (ethyl nitrite giving good yields) on a chloroform solution of pyromeconic acid. The action of phenylhydrazine on this substance gives rise to a mixture of two stereoisomeric *phenylosazones* of nitrosopyromeconic acid of the composition  $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}_5$ ; both these separate from xylene solution in yellow needles, the melting points being  $165^\circ$  and  $197^\circ$  respectively; both give yellow, slightly soluble xantho-compounds when treated with alkali, and after long boiling with hydrochloric acid they reduce Fehling's solution. On oxidation, these compounds yield the corresponding *osotetrazones*,  $\text{O} \cdot \text{C}(\text{NOH}) \cdot \text{C} \cdot \text{N} \cdot \text{NPh}$   
 $\text{CH} \cdot \text{CH} - \text{C} \cdot \text{N} \cdot \text{NPh}$ , and when heated above their melting points they lose water and yield one and the same *osotriazole derivative* having the constitution



and separating in white needles melting at  $242^\circ$ .

Pyromeconic acid reacts as a keto-compound with diazonium acetate,

yielding the *phenylhydrazone*,  $\text{CH} \begin{smallmatrix} \text{CH-O} \\ \text{CO} \cdot \text{CO} \end{smallmatrix} > \text{C} : \text{N}_2 \text{HPh}$ , which is deposited from xylene or alcohol in red needles melting and decomposing at  $175^\circ$ ; with excess of phenylhydrazine, this hydrazone yields a small quantity of an *isomeric* hydrazone also melting at  $175^\circ$ , but is mainly converted into a *triphenylhydrazone*,  $\text{CH} \begin{smallmatrix} \text{O-C(N}_2\text{HPh)} \\ \text{CH} \cdot \text{C(N}_2\text{HPh)} \end{smallmatrix} > \text{C} : \text{N}_2 \text{HPh}$ , which crystallises from dilute acetic acid in leaflets melting at  $158.5^\circ$ .  
T. H. P.

**Study of Ethyl Glutaconate.** By FERDINAND HENRICH (*Ber.*, 1902, 35, 1663—1667. Compare Abstr., 1898, i, 631).—Ethyl glutaconate, which contains a methylene group situated between a carbonyl radicle and an unsaturated double linking, resembles ethyl acetoacetate and other substances of this type. Its *sodium* derivative,  $\text{C}_9\text{H}_{13}\text{O}_4\text{Na}$ , readily obtained by heating the ethereal solution of ether with sodium, has an intensely yellow colour and appears to be stable for some time in aqueous solution.

The dimethylglutaric acid, obtained by reducing dimethylglutaconic acid with phosphorus and hydriodic acid, crystallises from benzene in druses melting at  $100$ — $101^\circ$ , and is not identical with the substance obtained by Blaise (*Bull. Soc. Chim.*, 1899, [iii], 21, 623) which melted at  $81^\circ$ .

On condensing the unsaturated ester with acetaldehyde in the presence of diethylamine, an oily substance is obtained boiling at  $150$ — $160^\circ$  under 14 mm. pressure, which gives figures approximating to the composition of *ethyl  $\alpha$ -ethylidenediglutaconate*; the product is, however, very unstable, and decomposes even when distilled under 5 mm. pressure. In this condensation, a very small quantity of a compound is produced having the composition of *ethyl  $\alpha$ -ethylidene-glutaconate*,  $\text{CO}_2\text{Et} \cdot \text{CH} : \text{CH} \cdot \text{C}(\text{CHMe}) \cdot \text{CO}_2\text{Et}$ .

*Potassium  $\alpha$ -benzylideneglutaconate* is prepared by condensing benzaldehyde and ethyl glutaconate in a methyl alcohol solution of potassium hydroxide; the *acid*,  $\text{CO}_2\text{H} \cdot \text{C}(\text{CHPh}) \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{H}$ , decomposes at  $161^\circ$  and is hydrolysed by dilute sulphuric acid. Similar condensation products are obtained from *p*-nitrobenzaldehyde and salicylaldehyde.

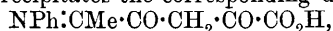
A *formazyl* derivative is produced by treating 1 mol. of ethyl glutaconate dissolved in dilute alcohol containing sodium acetate with 2 mols. of benzenediazonium chloride; it separates from benzene and light petroleum in ruby-red crystals with a metallic lustre and melts at  $117^\circ$ .  
G. T. M.

**Some Derivatives of Ethyl Pyruvylpyruvate.** By L. J. SIMON (*Compt. rend.*, 1902, 134, 1063—1065).—The compound

$\text{NPh} : \text{CMe} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C}(\text{CO}_2\text{Et}) : \text{NPh}$ , obtained by the action of aniline on ethyl pyruvate (Abstr., 1894, i, 509; 1896, i, 85), assumes a red colour when treated with sulphuric acid of sp. gr. 1.84. When the solution is poured on to ice, white crystals of the compound  $\text{NPh} : \text{CMe} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CO}_2\text{Et}$  are formed. This substance can be recrystallised from alcohol; it melts at

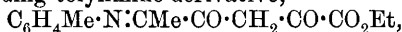


139—140°, is sparingly soluble in cold water, but easily so in the ordinary organic solvents, and particularly in pyridine. It is insoluble in dilute, but soluble without change in concentrated, acids. It is easily soluble in dilute potassium hydroxide, and acids reprecipitate it from the solution; it behaves, therefore, as an acid. By prolonged action of alkali, it suffers decomposition. When dissolved in excess of alkali and heated for a few minutes, it is hydrolysed, and dilute mineral acid then precipitates the corresponding diketonic acid,



as a white, crystalline substance which melts at 132—133° with decomposition. The acid is insoluble in water, but soluble in alcohol. Its silver salt deposits silver on heating. The hydrazone crystallises well and decomposes at 145°.

The corresponding tolylimino-derivative,



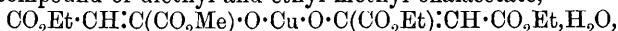
resembles the phenylimino-compound; it melts at 152°.

If sulphuric acid containing 25 to 50 per cent. of dissolved anhydride be employed, no precipitate is obtained on pouring on to ice, and it is presumed that the unknown ethyl pyruvylpyruvate is produced.

J. McC.

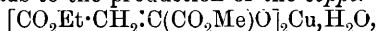
**Copper Derivative of Ethyl Oxalacetate.** By WILHELM WISLIGENUS and ANTON ENDRES (*Annalen*, 1902, 321, 372—385).—*Copper ethyl oxalacetate*,  $(\text{C}_8\text{H}_{11}\text{O}_5)_2\text{Cu}\cdot\text{H}_2\text{O}$ , prepared in a state of purity by slowly adding a concentrated aqueous solution of copper acetate to an alcoholic solution of ethyl oxalacetate and crystallising the product from absolute alcohol or benzene, is obtained in bright green needles melting at 155—156°. The hydrated substance, when repeatedly crystallised from benzene, loses its water of crystallisation and changes into bluish-green plates melting at 162—164°; these, however, regain their water on exposure to the atmosphere for several days.

On crystallising the copper derivative from methyl alcohol, a substitution of a methyl radicle for ethyl takes place, so that a mixed *copper* compound of diethyl and ethyl methyl oxalacetate,



is produced, this substance forming light green needles melting at 132—133°. This singular change does not occur with the diethyl oxalacetate itself, even on long boiling with methyl alcohol, the greater portion of the original ester being recovered; a similar negative result is obtained with the dimethyl ester and ethyl alcohol.

Prolonged boiling of the mixed copper derivative with excess of methyl alcohol leads to the production of the *copper* derivative,



of ethyl methyl oxalacetate, a compound crystallising in light green needles and melting at 165—166°. At 90°, this substance becomes anhydrous, and then melts at 173—174°; it yields methyl ethyl oxalacetate (*Abstr.*, 1894, i, 116) on treatment with dilute sulphuric acid, and methyl 1-phenyl-5-pyrazolone-3-carboxylate when condensed

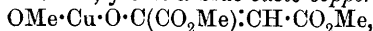
with phenylhydrazine; the latter reaction shows that the methyl group is attached to the oxaly radical.

The preceding copper compound, on prolonged boiling with absolute alcohol, is reconverted into the corresponding diethyl derivative.

The *basic copper* derivative,  $\text{OMe}\cdot\text{Cu}\cdot\text{O}\cdot\text{C}(\text{CO}_2\text{Me})\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , produced by boiling the anhydrous copper derivative of diethyl oxalacetate with a solution of sodium methoxide in absolute methyl alcohol, crystallises from this solvent in slender blue needles decomposing gradually above  $200^\circ$ . In the presence of water, this reaction takes another course, and a bluish-green, slimy precipitate containing both sodium and copper is obtained, which on treatment with acid yields the acid ester,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , a substance melting at  $102\text{--}103^\circ$ , and not at  $97\text{--}98^\circ$  as previously stated (*Annalen*, 1888, 246, 323). The formation of a basic copper derivative is not observed when alcohol and sodium ethoxide are employed.

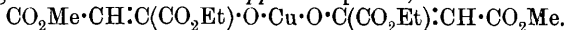
The preceding basic copper compound is extremely soluble in benzene. This solution on prolonged boiling turns green, and after concentration deposits the neutral copper derivative of the methyl ethyl ester.

The anhydrous copper derivative of dimethyl oxalacetate, when boiled with methyl alcohol, yields a blue *basic copper* compound,



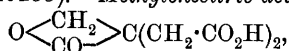
separating in slender needles and dissolving in benzene with the regeneration of the neutral substance.

The neutral copper derivative, on prolonged boiling with ethyl alcohol, gives rise to a mixed *copper* compound,



G. T. M.

**Methylenecitric Acid.** CHEMISCHE FABRIK AUF ACTIEN (FORM. E. SCHERING) (D.R.-P. 129255).—*Methylenecitric acid*,



prepared either by heating citric acid with paraformaldehyde at  $140\text{--}160^\circ$  or by condensing the acid with formaldehyde solution in the presence of hydrochloric or sulphuric acid, is sparingly soluble in cold water, but readily dissolves in the hot solvent; it melts at  $208^\circ$  and is stable towards acids, but decomposed by alkali hydroxides and carbonates.

G. T. M.

**l-Xylonic Acid.** By CARL NEUBERG (*Ber.*, 1902, 35, 1473—1475. Compare this vol., ii, 417).—*Brucine l-xylonate*,  $\text{C}_5\text{H}_{10}\text{O}_6\cdot\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2$ , prepared by neutralising an aqueous solution of the acid with brucine, crystallises in needles or rhombic plates melting at  $172\text{--}174^\circ$ , and has  $[\alpha]_D - 37\cdot65^\circ$  at  $15^\circ$  in aqueous solution; l-xylonic acid is readily separated from the other products of the hydrolysis of proteids in the form of this salt (*loc. cit.*). The *cinchonine* salt crystallises in elongated plates or needles melting and decomposing at  $180^\circ$ , and has  $[\alpha]_D 125\cdot0^\circ$  at  $17^\circ$  in aqueous solution; the *morphine* salt forms ill-defined needles melting at  $153^\circ$ . The *phenylhydrazide*,  $\text{C}_5\text{H}_9\text{O}_5\cdot\text{N}_2\text{H}_2\text{Ph}$ , crystallises in colourless needles melting and decomposing at  $129^\circ$ .

K. J. P. O.

**Formation of Aldehydes and Ketones from  $\beta$ -Chloro-alcohols.** By K. KRASSUSKY (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 287—315).—In a previous paper (this vol., i, 261), the author gave a scheme for the reactions occurring in the formation of aldehydes and ketones from haloid derivatives of olefines, according to which the first product formed is a halogen derivative of an alcohol. To test the truth of this assumption, an examination has been made of the products obtained by heating  $\beta$ -chloro-alcohols with water and the results are in accord with it.

Trimethylethylene chlorohydrin, when heated in a sealed tube with water, reacts as follows:  $\text{OH} \cdot \text{CMe}_2 \cdot \text{CHMeCl} = \text{CHMe}_2 \cdot \text{COMe} + \text{HCl}$ , and possibly also to a certain extent according to the equation:  $\text{CMe}_2\text{Cl} \cdot \text{CHMe} \cdot \text{OH} = \text{CHMe}_2 \cdot \text{COMe} + \text{HCl}$ . Other compounds studied were: Ethylene chlorohydrin, which is decomposed as follows:  $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Cl} = \text{CH}_3 \cdot \text{CHO} + \text{HCl}$ ; propylene chlorohydrin, which splits up in two ways,  $\text{OH} \cdot \text{CHMe} \cdot \text{CH}_2\text{Cl} = \text{COMe}_2 + \text{HCl}$  and  $\text{OH} \cdot \text{CHMe} \cdot \text{CH}_2\text{Cl} = \text{CH}_2\text{Me} \cdot \text{CHO} + \text{HCl}$ ; isobutylene chlorohydrin,  $\text{OH} \cdot \text{CMe}_2 \cdot \text{CH}_2\text{Cl} = \text{CHMe}_2 \cdot \text{CHO} + \text{HCl}$ ; hexylene chlorohydrin, which gives a ketone and hydrogen chloride; tetramethylethylene chlorohydrin,  $\text{OH} \cdot \text{CMe}_2 \cdot \text{CMe}_2\text{Cl} = \text{CH}_3 \cdot \text{CO} \cdot \text{CMe}_3 + \text{HCl}$ .

$\psi$ -Butylene chlorohydrin,  $\text{OH} \cdot \text{CHMe} \cdot \text{CHMeCl}$ , prepared by the action of hypochlorous acid on  $\psi$ -butylene, boils at  $136-137^\circ$  under 760 mm. pressure and has the sp. gr. 1.0868 and 1.0870 at  $0^\circ/0^\circ$  and 1.0692 at  $18^\circ/0^\circ$ . When treated with water, it decomposes according to the equation:  $\text{OH} \cdot \text{CHMe} \cdot \text{CHMeCl} = \text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2\text{Me} + \text{HCl}$ .

These chlorohydrins also split up in a similar manner when they are heated alone in sealed tubes.

On heating with water in presence of lead oxide, silver oxide, or zinc oxide, these chlorohydrins yield organic oxides, and these the author considers to be the primary product, the formation of glycols, aldehydes, or ketones being the result of the action of hydrochloric acid on the organic oxides. This secondary action the author is now investigating.

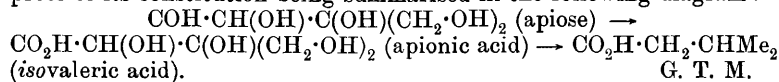
T. H. P.

**Apiose, a  $\beta$ -Hydroxymethylerythrose.** By EDUARD VONGERICHTEN (*Annalen*, 1902, 321, 71—83. Compare Abstr., 1901, i, 646).—When oxidised with bromine in aqueous solutions, apiose, the pentose derived from apiin, gives rise to a new tetrahydroxyvaleric acid to which the name *apionic acid* is given.

The *calcium* salt,  $(\text{CaC}_5\text{H}_9\text{O}_6)_2$ , of this acid is amorphous, the *strontium* salt,  $\text{Sr}(\text{C}_5\text{H}_9\text{O}_6)_2$ , is crystalline. The acid itself is a colourless syrup which yields a *phenylhydrazide*,  $\text{C}_{11}\text{H}_{16}\text{O}_5\text{N}_2$ , crystallising in small, white prisms melting at  $126-127^\circ$ .

The reduction of apionic acid with red phosphorus and hydriodic acid leads to the production of *isovaleric acid*, this substance being identified by means of its silver, calcium, and barium salts.

These results show that apiose is a  $\beta$ -hydroxymethylerythrose, the proof of its constitution being summarised in the following diagram:



G. T. M.

**Acetyl Derivatives of the Two Methylglucosides; Acetyl-bromodextrose.** By J. MOLL VAN CHARANTE (*Rec. Trav. Chim.*, 1902, [ii], 21, 42—44).—Tetra-acetyl- $\alpha$ -methylglucoside (Koenigs and Knorr, *Abstr.*, 1901, i, 369; Fischer and Armstrong, *ibid.*, 257) crystallises from benzene with  $1\text{C}_6\text{H}_6$ , which it loses on standing in the air; in solution in benzene, it has  $[\alpha]_D + 173^\circ 17'$  at  $20^\circ$ , whereas the benzene-free substance in alcohol has  $[\alpha]_D + 137^\circ 17'$  at  $20^\circ$ . Tetra-acetyl- $\beta$ -methylglucoside does not crystallise with benzene, and in alcoholic solution has  $[\alpha]_D - 27^\circ 20'$  at  $20^\circ$ .

For the preparation of acetyl-bromodextrose, the author finds it best to extract the mixture obtained on heating dextrose and acetyl bromide, thoroughly with water and dilute aqueous sodium carbonate, and finally to crystallise the product from ether, whence it separates in hard needles (m. p.  $88-89^\circ$ ).

K. J. P. O.

**Extraction of Reducing Sugars (Monoses).** By CHARLES TANRET (*Bull. Soc. Chim.*, 1902, [iii], 27, 392—398).—For the purpose of separating and identifying monoses when mixed with hydrolysable sugars, the author recommends the conversion of the sugars into their phenylhydrazones and the separation of these by means of their varying solubilities in ethyl acetate. Thus the phenylhydrazones of lactose and maltose are only slightly soluble in ethyl acetate, whilst those of dextrose and lævulose are fairly readily soluble; it has therefore been found possible to separate from a mixture of these 77—92 per cent. of the monoses.

The author has studied the action of phenylhydrazine on several of the monoses with the view of ascertaining the amount of phenylhydrazones formed under certain conditions and their solubilities, and has prepared *arabinose phenylhydrazone* for the first time. This forms slender, white needles, melts at  $153^\circ$ , and is feebly dextrorotatory.

A. F.

**The Swelling and Solution of Starch by Chloral Hydrate and the Influence of Chloral Hydrate on the Retardation or Prevention of the Iodine Starch Reaction.** By RICHARD MAUCH (*Arch. Pharm.*, 1902, 240, 166—178. Compare this vol., i, 344).—Solutions of chloral hydrate only cause starch to swell and dissolve when they contain 40—70 per cent. of chloral hydrate; an 80 per cent. solution does not act in this way until a temperature of nearly  $100^\circ$  is reached. The solution contains amylo-dextrin and amylogen, traces of dextrin at most, and no dextrose. The different kinds of starch behave in somewhat different ways.

A solution of starch in chloral hydrate solution reacts comparatively slowly with iodine, and does not react at all when the percentage of chloral hydrate present exceeds 70. A solution of iodine in 80 per cent. chloral hydrate solution does not colour dry starch grains, solutions containing 70 per cent. or less of chloral hydrate do colour the grains.

A list of cases is given in which a 60—80 per cent. aqueous solution of chloral hydrate may be employed advantageously in analysis.

C. F. B.

**Transformation of New Bread into Old.** By LEON LINDET (*Compt. rend.*, 1902, 134, 908—910).—When bread is allowed to become stale, the only change occurring in the crust is one of hydration; there is no alteration in the proportion of soluble dextrin, and the starch present is as capable of absorbing water after 48 hours as when the loaf is taken out of the oven. On the other hand, very marked changes take place in the composition of the crumb, the percentage of soluble amylodextrin falls from 10 to 2 per cent.; the starch becomes less soluble in dilute acid and less capable of absorbing water; these chemical changes correspond with the increase in the friability of the crumb.

The communication includes a table of numerical data referring to the estimation of the dextrin and insoluble starch and the ratio between the volumes of the latter substance before and after hydration; this quantity, which is taken to be the coefficient of absorption, is constant for the crust but falls from 6·7 to 2·8 for the crumb.

G. T. M.

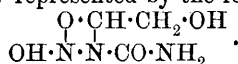
[Attempt to prepare] **Derivatives of Methylenediamine.** By RICHARD KUDERNATSCHEK (*Monatsh.*, 1902, 23, 119—122).—Methylene chloride does not react with benzenesulphonethylamide, and with its sodium derivative only in the complete absence of water and alcohol. No diethylmethylenediamine could be obtained. The product on treatment with concentrated hydrochloric acid yielded methylamine hydrochloride, and on distillation phenyl disulphide and a residue which on warming with alkali gave only a weak amine odour.

G. Y.

**Nitroamino-alcohols.** By ANTOINE P. N. FRANCHIMONT and A. LUBLIN (*Rec. Trav. Chim.*, 1902, 21, 45—55).—A more detailed account of work previously published (*Abstr.*, 1901, i, 674).

Ethyl  $\beta$ -hydroxyethylaminoformate ( $\beta$ -hydroxyethylcarbamate) boils at 152° under 12 mm., and at 163° under 16 mm. pressure.

The character of hydroxyethylnitrocarbamide (*loc. cit.*) suggests that it is more appropriately represented by the formula



The internal anhydride of hydroxypropylcarbamic acid is prepared from bromopropylphthalimide, and on nitration yields 2-keto-1-nitropentoxazolidine,  $\text{NO}_2 \cdot \text{N} \langle \text{CH}_2 \cdot \text{CH}_2 \rangle \text{CH}_2$ , which crystallises in colourless leaflets melting at 74°; when boiled with water, it decomposes into carbon dioxide and an oily substance.

K. J. P. O.

**Improved Method for the Preparation of Betaine.** By VL. STANEK (*Zeit. Zuckerind. Böhm.*, 1902, 26, 287—289).—Concentrated sulphuric acid, when heated with betaine for 5 hours at 120°, or for 3 hours at 130°, has but slight action on it, whilst under the same conditions sucrose and asparagine undergo complete decomposition. The author's method, based on this marked stability of betaine, is as follows: Equal quantities of either molasses or osmose liquors of sp. gr. 85° Baumé from the manufacture of beet sugar and

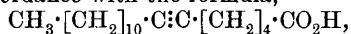
concentrated sulphuric acid are mixed in a large flask, and when the first violent reaction is over the mass is heated at 120—130° for 3 hours, then stirred up with water and made alkaline with calcium hydroxide. The liquid is then evaporated to dryness and the powdered residue repeatedly extracted with boiling alcohol, by which means almost the whole of the betaine is brought into solution. After boiling with spodium, the liquid is filtered and the alcohol distilled off. The residual solution may then be well cooled and treated with a current of hydrogen chloride, or it may be evaporated to a syrup to deposit betaine, which is removed, the mother liquor, after dilution with double its volume of alcohol, being then treated with hydrogen chloride. The betaine hydrochloride obtained in either of these ways is recrystallised from water or dilute alcohol. Satisfactory yields are obtained by this method.

T. H. P.

**Betaine Aurichloride.** By EMIL FISCHER (*Ber.*, 1902, 35, 1593—1595).—Contrary to Willstätter's statement (this vol., i, 266), betaine aurichloride is partially decomposed when crystallised from water, and can only be obtained pure by crystallisation from dilute hydrochloric acid; it then melts, when rapidly heated, at 245° (250° corr.), not at 209°.

W. A. D.

**Products of Decomposition of Aminotariric Acids.** By ALBERT ARNAUD (*Compt. rend.*, 1902, 134, 842—843. Compare this vol., i, 342, 343).—The oxime of ketotariric acid (*loc. cit.*) yields a mixture of two aminotariric acids (denoted as  $\alpha$  and  $\beta$ ) when heated with concentrated sulphuric acid at 100°. This mixture crystallises in white needles melting at 75—76°, and when heated under pressure at 170° with fuming hydrochloric acid gives four substances.  $\alpha$ -Aminotariric acid,  $C_{11}H_{23}\cdot NH\cdot CO\cdot [CH_2]_5\cdot CO_2H$ , breaks up into undecylamine,  $C_{11}H_{23}\cdot NH_2$  and pimelic acid,  $C_5H_{10}(CO_2H)_2$ ; whereas  $\beta$ -aminotariric acid,  $C_{11}H_{23}\cdot CO\cdot NH\cdot [CH_2]_5\cdot CO_2H$ , yields lauric acid,  $C_{11}H_{23}\cdot CO_2H$ , and  $\epsilon$ -aminohexoic acid,  $NH_2\cdot [CH_2]_5\cdot CO_2H$ . These reactions are in accordance with the formula,



previously suggested for tariric acid (*loc. cit.*).

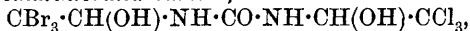
K. J. P. O.

**Sulphamides and Sulphanilides of the Aliphatic Series.** By DUGUER (*Rec. Trav. Chim.*, 1902, [ii], 21, 75—86).—*Propylsulphonic chloride*,  $CH_3Me\cdot CH_2\cdot SO_2Cl$ , prepared from potassium propylsulphonate and phosphorus pentachloride, is a mobile liquid which boils at 77.5—78° under 13 mm., and at 180° with decomposition under ordinary pressure, and has a sp. gr. 1.2996 at 0°/4°; in dry ethereal solution, with dry ammonia, it gives *propylsulphonamide*, which crystallises in long prisms or leaflets melting at 52°; the corresponding *anilide* melts at -10°.

*isoButylsulphonic chloride* boils at 79.5—80° and *isoamylsulphonic chloride* at 97.5—98° under 13 mm. pressure. *isoButylsulphonamide*,  $C_4H_9\cdot SO_2\cdot NH_2$ , melts at 14—16°; *isobutylsulphonanilide* crystallises in white needles melting at 38—38.5°. *isoAmylsulphonamide* melts at 3°, and the corresponding *anilide* at 42°.

Methylsulphon-amide and -anilide melt respectively at 90° and 99°, and ethylsulphonanilide melts at 58°. K. J. P. O.

**Bromalchloralcarbamide.** KALLE & Co. (D.R.-P. 128462).—Carbamide, when mixed with molecular proportions of chloral and bromal or when heated with the corresponding quantities of their hydrates in the presence of concentrated hydrochloric or sulphuric acid, yields *bromalchloralcarbamide*,



a substance separating in small crystals, decomposing at 186° and dissolving readily in ether or the alcohols. The solution of this compound in sodium or potassium hydroxide evolves bromoform and chloroform on gently warming, or even when left at the ordinary temperature. Neutral silver nitrate solution has no action on the compound, even on boiling, but the ammoniacal solution is immediately reduced.

G. T. M.

**Composition of Commercial Potassium Cyanide.** By RUSSELL W. MOORE (*J. Soc. Chem. Ind.*, 1902, 21, 392—393).—Out of 85 samples of potassium cyanide of various brands, only 24 were free from sodium cyanide, whilst one was entirely composed of that salt. In the other samples, the percentage of sodium cyanide varied from 9·84 to 54·49. W. P. S.

**Ferrocyanides of Cadmium.** By EDMUND H. MILLER (*J. Amer. Chem. Soc.*, 1902, 24, 226—234).—It has been shown (Miller and Fisher, *Abstr.*, 1900, ii, 761) that the results obtained on titrating neutral or slightly acid solutions of cadmium with potassium ferrocyanide do not agree with any of the formulæ given for the precipitate, whilst the values obtained with an ammoniacal solution agree closely with those required for the formula  $\text{K}_2\text{CdFe}(\text{CN})_6$ . A study has been made of the composition of the precipitate obtained under various conditions.

When the ferrocyanide is in excess, the precipitate from either an ammoniacal or acid solution has the composition  $\text{K}_2\text{CdFe}(\text{CN})_6$ , whilst that obtained from a neutral solution contains a larger proportion of cadmium.

When the cadmium is in excess, the composition of the precipitate formed in a neutral solution or in presence of hydrochloric acid corresponds with  $\text{K}_8\text{Cd}_{10}[\text{Fe}(\text{CN})_6]_7$ , whilst in a solution containing acetic acid it corresponds with  $\text{K}_6\text{Cd}_7[\text{Fe}(\text{CN})_6]_5$ .

If, in an ammoniacal solution with cadmium in excess, the suspended precipitate is decanted from that which has subsided, the former has the composition  $\text{K}_2\text{CdFe}(\text{CN})_6$ , and the latter  $\text{K}_2\text{Cd}_3[\text{Fe}(\text{CN})_6]_2$ ; by repeatedly washing the precipitate  $\text{K}_2\text{Cd}_3[\text{Fe}(\text{CN})_6]_2$  with strong ammonia, a residue is obtained of the composition  $\text{Cd}_2\text{Fe}(\text{CN})_6$ . These experiments show that the original precipitate is a mixture of two simple ferrocyanides,  $\text{Cd}_2\text{Fe}(\text{CN})_6$  and  $\text{K}_2\text{CdFe}(\text{CN})_6$ . Similar examination of the precipitates obtained from acid solutions indicate that these are also mixtures (or very easily decomposable double salts) of the same two ferrocyanides. E. G.

**Reactions of Amidoximes.** By HUGO SCHIFF (*Annalen*, 1902, 321, 357—371).—The substance obtained by hydrolysing oxamethane

with hydroxylamine (Schiff and Monsacchi, Abstr., 1896, i, 209), and reinvestigated by Hollemann (Abstr., 1897, i, 23), is now considered to be aminoximino-oxalic acid,  $\text{OH}\cdot\text{N}:\text{C}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ ; it is very slightly acid until the basic function of the amino-radicle has been masked by formaldehyde (compare this vol., i, 85), after which it behaves as a monobasic acid, this reaction being due entirely to the carboxyl group, and not to the *isonitroso*-radicle.

Amino-oximinomalonic acid,  $\text{OH}\cdot\text{N}:\text{C}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (Modeen, Abstr., 1892, i, 139, and Pinner and Oppenheimer, Abstr., 1895, i, 266), also behaves as a monobasic acid in the presence of formaldehyde; its

*copper* salt,  $\text{NH}_2\cdot\text{C}\begin{smallmatrix} \text{CH}_2\cdot\text{CO} \\ \text{NO}-\text{Cu} \end{smallmatrix}$ , is a dark green, granular substance.

Hydroxamoximinomalonic acid,  $\text{OH}\cdot\text{N}:\text{C}(\text{NH}\cdot\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (Hantzsch and Urbahn, Abstr., 1895, i, 393), behaves as a dibasic acid, the acid character being due to the carboxyl and *isonitroso*-groups; the addition of formaldehyde to the neutralised solution causes the mixture to become alkaline; this exceptional behaviour is probably due to the removal of the alkali radicle from the oxime group, owing to the interaction of the latter with formaldehyde. The free acid melts at  $144-145^\circ$  (compare Hantzsch and Urbahn, *loc. cit.*), and yields a green *copper* salt,  $\text{Cu}[\text{O}:\text{N}:\text{C}(\text{NH}\cdot\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{Cu}\cdot\text{OH}]_2$ .

The formation of the flocculent, green *copper* derivatives is a characteristic property of the amino-oximes, and the communication contains a summary of the compound of this type giving distinctive reactions with *copper* salts.

*Oximinolactamide*,  $\text{OH}\cdot\text{CHMe}\cdot\text{C}(\text{NH}_2):\text{N}\cdot\text{OH}$ , and the succeeding amino-oximes are all obtained by treating the corresponding cyanohydrins with hydroxylamine hydrochloride and sodium carbonate in aqueous solutions; it crystallises from ethyl acetate in colourless plates melting at  $115-116^\circ$ ; its *benzoyl* derivative melts at  $188-189^\circ$ .

*Oximino- $\alpha$ -hydroxyhexoamide*,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{C}(\text{NH}_2)_2:\text{NOH}$ , produced from *isovaleraldehyde* cyanohydrin, crystallises from water or ether, melts at  $176.5^\circ$ , and yields a green *copper* derivative.

*Oximino- $\alpha$ -hydroxyoctoamide*,  $\text{C}_6\text{H}_{13}\cdot\text{CH}(\text{OH})\cdot\text{C}(\text{NH}_2)_2:\text{NOH}$ , derived from *œnanthaldehyde* cyanohydrin, separates from dilute methyl alcohol in leaflets melting at  $141^\circ$ , the *benzoyl* derivative melts at  $143^\circ$ .

*Oximino- $\alpha$ -hydroxybutyramide*,  $\text{OH}\cdot\text{CMe}_2\cdot\text{C}(\text{NH}_2):\text{N}\cdot\text{OH}$ , prepared from acetone cyanohydrin, ammonium hypochlorite, and ammonium or sodium carbonate, crystallises from anhydrous ether in colourless needles melting at  $51-52^\circ$  and subliming at  $55-60^\circ$ ; it gives an intense reddish-violet coloration with alkaline *copper* solutions. The amino-oxime is, however, very unstable, and after six months loses this characteristic property.

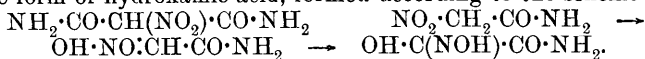
*Oximinotrichlorolactamide*,  $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{C}(\text{NH}_2):\text{NOH}$ , melts at  $156-157^\circ$  and not at  $145^\circ$  (compare Richter, Abstr., 1892, 321); it forms a green *copper* derivative,  $\text{C}_3\text{H}_3\text{O}_2\text{N}_2\text{Cl}_3(\text{Cu}\cdot\text{OH})_2$ .

G. T. M.

Transformation of Nitro-derivatives into Hydroxamic Acids. By C. ULPANI and C. FERRETTI (*Gazzetta*, 1902, 32, i, 205-217).—The action of concentrated sulphuric acid on nitromalonamide yields



two products: (1) a small quantity of a white, crystalline compound,  $C_2H_2O_2N_2$ , melting at  $216^\circ$  and slightly soluble in water or alcohol; (2) a compound,  $C_2H_4O_3N_2$ , identical with that obtained by Schiff and Monsacchi (Abstr., 1896, i, 209), which the author shows to be the stable form of hydroxamic acid, formed according to the scheme:



Its ammonium and mercury salts were prepared and analysed. On hydrolysis, the acid yields oxamic acid, oxalic acid, and ammonium hydrogen oxalate. See also Holleman (Abstr., 1897, i, 23).

T. H. P.

**Hydroxyisopropylphosphinic Acid.** By CH. MARIE (*Compt. rend.*, 1902, 134, 847—849. Compare Abstr., 1901, i, 635, and this vol., i, 255).—*Hydroxyisopropylphosphinic acid* ( $H_3PO_3, C_3H_6O$ ) is most conveniently prepared from hydroxyisopropylhypophosphorous acid (*loc. cit.*), which is oxidised in aqueous solution by a slight excess of mercuric chloride. After removing the excess of mercuric salt by hydrogen sulphide, and the hydrochloric acid by evaporation, the acid is purified by recrystallisation from acetic acid. Other oxidising agents may be used, but hydroxyisopropylhypophosphorous acid cannot be oxidised electrolytically.

Hydroxyisopropylphosphinic acid forms small, white crystals, melting at  $175^\circ$  (compare *loc. cit.*), which are stable in the air. It slowly decomposes at  $150$ — $160^\circ$ , but only completely at  $250^\circ$ . Prolonged ebullition with hydrochloric acid slowly converts it into acetone and phosphorous acid; boiling alkali hydroxides are without effect. In the presence of methyl-orange, it behaves as a monobasic acid, but in the presence of phenolphthalein as a dibasic acid. It is not a reducing agent. Its calcium, barium, and strontium salts are crystalline, and more soluble in cold than in hot water. The silver and lead salts are insoluble crystalline precipitates.

K. J. P. O.

**Salts of Hydroxyisopropylphosphinic Acid.** By CH. MARIE (*Compt. rend.*, 1902, 134, 994—995).—Hydroxyisopropylphosphinic acid (preceding abstract), gives normal and hydrogen salts. The normal sodium salt,  $Na_2HPO_3, C_3H_6O, 5H_2O$ , is obtained as crystals which lose water at  $100^\circ$  and decompose at  $210$ — $220^\circ$ ; it is extremely soluble in water, and is not precipitated by alcohol. The sodium hydrogen salt,  $NaH_2PO_3, C_3H_6O, 6H_2O$ , is prepared by neutralising the acid with sodium hydroxide (using methyl-orange as indicator) and precipitating with alcohol; the salt effloresces and loses its water completely at  $100^\circ$ . At this temperature also acetone is evolved and the decomposition takes place according to the equation:  $2NaH_2PO_3, C_3H_6O = Na_2H_2P_2O_5, C_3H_6O + H_2O + C_3H_6O$ . When the normal sodium salt is treated with a solution of a lead salt, it gives a precipitate of  $PbHPO_3, C_3H_6O$ , which is sparingly soluble in water but very easily soluble in nitric acid. On treating the free acid with excess of copper carbonate and precipitating with alcohol, the compound  $Cu(H_2PO_3, C_3H_6O)_2, 2C_2H_6O$  is obtained; this loses its alcohol slowly at the ordinary temperature and rapidly at  $100^\circ$ , giving  $Cu(H_2PO_3, C_3H_6O)_2$ .

The *copper hydrogensalt* with alcohol of crystallisation, when dissolved in warm water, decomposes, alcohol being evolved and the normal salt,  $\text{CuHPO}_3 \cdot \text{C}_3\text{H}_6\text{O} \cdot \text{H}_2\text{O}$  precipitated; this loses water completely at  $150^\circ$ . The *silver salt*,  $\text{Ag}_2\text{HPO}_3 \cdot \text{C}_3\text{H}_6\text{O}$ , is obtained as white, stable crystals by precipitation. Attempts to prepare a silver hydrogen and a lead hydrogen salt have invariably led to the production of the normal salts.

J. MCC.

**Cacodylic Acid and its Compounds.** By GIUSEPPE SIBONI (*Chem. Centr.*, 1902, i, 744; from *Boll. Chim. Farm.*, 41, 73—82).—The sodium, potassium, lithium, silver, calcium, barium, mercury, and iron salts of cacodylic acid are described in the original paper, together in some cases with details of their preparation and of methods of testing them. The commercial sodium salt usually contains  $2-3\text{H}_2\text{O}$ . The ferrous salt is easily converted into the ferric salt; its solutions give a green coloration with citric acid which is not affected by evaporation, and the residue, after removing the citric acid by absolute alcohol, gives the reactions of ferrous and ferric salts. *Codeine cacodylate*,  $\text{AsMe}_2\text{O} \cdot \text{OH} \cdot \text{C}_{18}\text{H}_{21}\text{O}_3\text{N}$ , prepared by treating barium cacodylate with an excess of codeine sulphate, forms a rather hygroscopic, reddish-white, crystalline powder, and is very readily soluble in water or alcohol, but only slightly so in ether; its solutions are neutral to phenolphthalein, but alkaline to helianthin and litmus. By the action of potassium permanganate, it gradually becomes yellow, and ultimately forms a brown precipitate; with copper sulphate, it slowly gives a bluish-white precipitate in the cold, but with hot solutions the precipitate is formed immediately. Codeine cacodylate gives the codeine reaction with sulphuric acid and ferric chloride, and with ferrous sulphate solutions a bluish-green precipitate is obtained. The therapeutic application of the salts of cacodylic acid and their compounds, and the various methods of using them, are also discussed in the original paper.

E. W. W.

**Oxidation of the Methyl Groups of Aromatic Hydrocarbons.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 127388).—Nickelic or cobaltic oxide may be employed in oxidising toluene, the xylenes, or nitrotoluene to the corresponding aldehyde and acid, the yield of the latter product being diminished by performing the operation in the presence of a nickel salt or of a small amount of acid.

Toluene, when heated at  $100^\circ$  with dry nickelic oxide, yields benzaldehyde; *o*-nitrotoluene, when mixed with the oxide and nickelous chloride and distilled in a current of steam, yields a distillate containing *o*-nitrobenzaldehyde and unaltered substance; the residue contains *o*-nitrobenzoic acid. The nickelous oxide resulting from this action is continuously reconverted into the higher oxide by slowly adding to the heated mixture a 10 per cent. solution of sodium hypochlorite.

G. T. M.

***s*- and *as*-Triethylbenzene.** By AUGUST KLAGES (*J. pr. Chem.*, 1902, [ii], 65, 394—400. Compare *Abstr.*, 1899, i, 598).—To separate *s*-triethylbenzene from *as*-triethylbenzene, the mixture is

sulphonated and warmed with phosphoric acid, when *s*-triethylbenzenesulphonic acid is decomposed into the hydrocarbon and sulphuric acid, the *as*-triethylbenzenesulphonic acid remaining unchanged. *s*-Triethylbenzenesulphonic acid is an oil; it forms a sodium salt, which is soluble in water or ether and is decomposed into the hydrocarbon and sodium sulphate by treatment with alcohol or by heating at 80°.

The *chloride* boils at 183° under 25 mm. pressure, and has the sp. gr. 1.146 at 25°; the *amide* crystallises in colourless needles melting at 118.5°, and the *anilide* separates from dilute alcohol in brittle needles melting at 128°. *s*-Triethyliodobenzene, prepared by Klages and Liecke's method (Abstr., 1900, i, 387), is a colourless oil, which boils at 149–150° under 12 mm. pressure and has the sp. gr. 1.44 at 15°.

*as*-Triethylbenzene, obtained by heating the sodium sulphonate with hydrochloric acid at 140°, is a colourless oil which boils at 216–218°. The sulphonic acid forms a *barium* salt, an insoluble *magnesium* salt, a *chloride*, which is an oil boiling at 202–204° under 32 mm. pressure and has sp. gr. 1.183 at 25°, an *amide*, which forms glistening needles melting at 111°, and an *anilide*, which crystallises in rhombic plates melting at 108°. G. Y.

**Methoethenylbenzene [ $\beta$ -Allylbenzene].** By MARC TIFFENEAU (*Compt. rend.*, 1902, 134, 845–847).—Methoethenylbenzene [ $\beta$ -allylbenzene; *as*-phenylmethylethylene],  $\text{CH}_2\text{:CMePh}$ , is formed in small amount when phenyldimethylcarbinol is heated at its boiling point; on dehydrating the carbinol with acetic anhydride or anhydrous oxalic acid, a mixture is obtained from which the hydrocarbon can be isolated by fractionation and treatment with sodium.  $\beta$ -Allylbenzene is an oil boiling at 160–162°, and has a sp. gr. 0.9231 at 0°; it is quantitatively converted into isopropylbenzene by sodium and boiling alcohol. By aqueous potassium permanganate, it is oxidised to acetophenone and acetic and formic acids. It forms a *dibromide*, which is an oil boiling at 115° under 8 mm. pressure. By potassium acetate, the dibromide is converted into an unsaturated *monobromide*,  $\text{C}_9\text{H}_9\text{Br}$ , but when boiled with water and barium carbonate, a *glycol* is obtained, melting at 37–38° and identical with that formed by the action of magnesium methiodide on benzylcarbinol or on benzylcarbiny acetate. The glycol is converted by sulphuric acid into  $\beta$ -phenylpropaldehyde, the *semicarbazone* of which melts at 203–204°. The iodohydrin, obtained from  $\beta$ -allylbenzene by the action of iodine and mercuric oxide, is converted by silver nitrate into benzyl methyl ketone, a transformation in which the phenyl group wanders from the  $\beta$ - to the  $\alpha$ -carbon atom. K. J. P. O.

**Chemical Action of Light. III.** By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Atti R. Accad. Lincei*, 1902, [v], 11, i, 277–284. Compare Abstr., 1901, i, 329 and 390).—A solution of 60 grams of nitrobenzene in 200 c.c. of absolute alcohol was exposed to the action of light during the whole summer, after which 50 grams of unaltered nitrobenzene was recovered, the remaining compounds yielding 6.6 grams of a mixture of hydrochlorides. From the latter were separated:

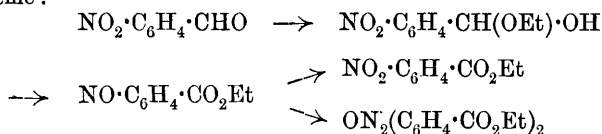
quinaldine; a small quantity of aniline admixed with another substance which on boiling with acetic anhydride gave a compound melting at  $174-175^{\circ}$ ; a tertiary *base* giving a picrate melting at  $168-169^{\circ}$ ; a small quantity of an aldehydic substance. The primary reaction between the nitrobenzene and alcohol probably yields aniline and acetaldehyde, the latter, by its condensation and its reaction with aniline, then giving rise to the other products found.

*m*-Nitrotoluene (10 grams in 50 c.c. of absolute alcohol) yielded the corresponding methylquinaldine and *m*-toluidine; the other nitro-toluenes give similar products. No appreciable quantity of basic substances could be obtained from *o*- and *m*-dinitrobenzenes, the three nitroanilines or nitronaphthalene.

*o*-Nitropiperonaldehyde in benzene solution yields *o*-nitrosopiperonylic acid by molecular rearrangement; *o*-nitrocinnamaldehyde remains unchanged.

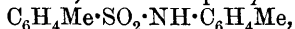
In benzene solution, *o*-nitrosobenzoic acid does not undergo change, but *o*-nitrobenzaldehyde yields a considerable proportion of *o*-nitrosobenzoic acid. In methyl or ethyl alcoholic solution, however, *o*-nitrobenzaldehyde or ethyl *o*-nitrosobenzoate yields a complex mixture of products, among which are *o*-azoxybenzenedicarboxylic acid and its diethyl ester and probably traces of ethyl anthranilate.

The transformation of *o*-nitrobenzaldehyde in alcoholic solution under the action of light takes place mainly according to the following scheme:



T. H. P.

**Preparation and Nitration of Derivatives of Toluene-*p*-sulphonic Chloride.** By FRÉDÉRIC REVERDIN and PIERRE CRÉPIEUX (*Ber.*, 1902, 35, 1439—1444).—*Toluene-p-sulphon-o-toluidide*,



crystallises from dilute acetic acid in white needles and melts at  $108^{\circ}$ . The *mononitro*-derivative crystallises from dilute acetic acid in yellow needles and melts at  $174^{\circ}$ ; it is hydrolysed to 5-nitro-1:2-toluidine. Other nitro-derivatives in the mother liquor gave on hydrolysis 3-nitro-1:2-toluidine and 3:5-dinitro-1:2-toluidine.

By the action of nitric acid on toluene-*p*-sulphon-*p*-toluidide, the *nitro*-derivative,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NO}_2$  [ $\text{Me} : \text{NH} : \text{NO}_2 = 1 : 4 : 3$ ], which melts at  $145-146^{\circ}$  is obtained; it is hydrolysed to 3-nitro-1:4-toluidine.

*Toluene-p-sulphondiphenylamide*,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_2 \cdot \text{NPh}_2$ , crystallises from alcohol or dilute acetic acid in white needles and melts at  $141^{\circ}$ . The *p*-dinitro-derivative,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_2 \cdot \text{N}(\text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$ , forms pearly flakes and melts at  $167-168^{\circ}$ , but a more soluble *o*-dinitro-derivative is also formed.

*Phenyl p-toluenesulphonate*,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_3\text{Ph}$ , forms white needles and melts at  $95-96^{\circ}$ . On nitration, it gives the *p*-nitro-ether.

*Phenyl o-nitrotoluene-p-sulphonate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_3\text{Ph}$ , forms white needles and melts at  $59-60^\circ$ .

*o-Tolyl p-toluenesulphonate*,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_3 \cdot \text{C}_6\text{H}_4\text{Me}$ , forms long, white needles and melts at  $54-55^\circ$ . The *dinitro*-derivative,

$\text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_3 \cdot \text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2$  [ $\text{Me} : (\text{NO}_2)_2 : \text{OH} = 1 : 3 : 5 : 2$ ], crystallises from alcohol and melts at  $108-109^\circ$ . The 6-mononitro-derivative was also produced but not hydrolysed. The *m-tolyl* ester crystallises in white needles and melts at  $51^\circ$ . The *p-tolyl* ester melts at  $69-70^\circ$ .

*o-Tolyl o-nitrotoluene-p-sulphonate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_3 \cdot \text{C}_6\text{H}_4\text{Me}$ , crystallises in white needles and melts at  $68-69^\circ$ . The *m-tolyl* ester melts at  $63^\circ$  and the *p-tolyl* ester at  $95^\circ$ .  
T. M. L.

Dimethylindenes contained in Tar. By JOHANNES BOES (*Chem. Centr.*, 1902, i, 811; from *Ber. Deut. pharm. Ges.*, 12, 84-86).—The dimethylindenes contained in tar have been isolated from the fraction boiling at  $220-230^\circ$  and their constitution determined by converting them into the corresponding benzenetetracarboxylic acids, prehnitic, mellphanic, and pyromellitic acids respectively. Assuming that all the six possible isomerides are present, then from the quantity of acid obtained it may be inferred that the tar contains the largest proportion of 4:6- and 5:7-dimethylindene, a less amount of 4:5-, 4:7-, and 6:7-dimethylindene, and a minimum of 5:6-dimethylindene.  
E. W. W.

**2:2'-Dinitrodiphenyl and its Derivatives.** FRITZ ULLMANN (D.R.-P. 126961).—*o*-Nitroaniline and its derivatives, when diazotised and treated with cuprous chloride, either in solution or suspension, give rise to diphenyl substitution products.

2:2'-Dinitrodiphenyl (compare Täuber, *Abstr.*, 1892, 480) is readily obtained from *o*-nitroaniline.

2:2'-Dinitro-4:4'-ditolyl, prepared from *m*-nitro-*p*-toluidine (m. p.  $114^\circ$ ), crystallises from glacial acetic acid or benzene in yellowish-brown leaflets and melts at  $139^\circ$ .

4:4'-Dichloro-2:2'-dinitrodiphenyl and 5:5'-dichloro-2:2'-dinitrodiphenyl, obtained respectively from *p*-chloro-*o*-nitroaniline and *m*-chloro-*o*-nitroaniline, crystallise in brown needles melting at  $136^\circ$  and  $170^\circ$ . They dissolve readily in acetic acid, but only sparingly in alcohol.

2:2'-Dinitrodiphenyl-4:4'-disulphonic acid, produced from ammonium *o*-nitroaniline-*p*-sulphonate, is isolated as a brown mass; its *potassium* salt is very soluble in water, but dissolves only sparingly in boiling alcohol.  
G. T. M.

***s.o.p*-Dinitrodiphenylmethane.** By KARL SCHORLEMMER (*J. pr. Chem.*, 1902, [ii], 65, 305-307). *o*-Nitrobenzophenone. By ALEXANDER VON TATSCHLOFF (*ibid.*, 308-310). *s.o.p*-Diaminobenzophenone. By OTTO BENOHR (*ibid.*, 310-313).—The purification, by distillation with steam, of *o*-nitrodiphenylmethane, prepared from *o*-nitrobenzyl chloride and benzene, is unnecessary before the preparation of its derivatives by nitration or oxidation (compare *Abstr.*, 1885, 1236, and 1895, i, 232, 233). 2:4'-Diaminobenzo  
i i 2

phenone yields a *hydrobromide*,  $C_{13}H_{12}ON_2 \cdot 2HBr$ , and a *diacetyl* derivative which melts at  $170^\circ$ . G. Y.

**s-Di-o-nitrodiphenylmethane.** By KARL SCHNITZSPAHN (*J. pr. Chem.*, 1902, [ii], 65, 315—326).—Crude 4 : 4'-diaminodiphenylmethane is best purified by fractional precipitation from a solution of its hydrochloride. Nitration leads to 2 : 2'-dinitro-4 : 4'-diaminodiphenylmethane, which melts at  $205^\circ$  (compare Abstr., 1892, 618). Its *sulphate* forms white needles easily soluble in alcohol. Its hydrochloride contains  $2\frac{1}{2}H_2O$ . When diazotised and boiled with alcohol, it yields 2 : 2'-*dinitrodiphenylmethane*, which forms slightly yellow leaflets melting at  $159^\circ$ , and a small amount of needles which melt at  $116^\circ$ , and are converted into dinitrodiphenylmethane by heating at  $100^\circ$ , or by solution in alkali and precipitation by an acid.

2 : 2'-Dinitrodiphenylmethane is easily soluble in alcohol, ether, glacial acetic acid, or ethyl acetate. It is easily soluble in dilute alkalis, and is reprecipitated unchanged by acids. On boiling the alkaline solution, alkali nitrite is formed, and on acidification a brown, amorphous substance is precipitated.

Oxidation of 2 : 2'-dinitrodiphenylmethane by chromic acid in glacial acetic acid solution leads to the formation of 2 : 2'-dinitrobenzophenone. Reduction by stannous chloride yields 2 : 2'-diaminodiphenylmethane, which forms white needles melting at  $160^\circ$ . G. Y.

**Di-o-nitrodiphenylmethane and Di-o-nitrobenzophenone.** By W. BERTRAM (*J. pr. Chem.*, 1902, [ii], 65, 327—345).—2 : 2'-Dinitrodiphenylmethane (m. p.  $158.5$ — $159.5^\circ$ ) gives a blood-red colour with a drop of concentrated sodium hydroxide solution, and dissolves completely on dilution with water. The product obtained by boiling with alkali and addition of acid melts at  $186$ — $189^\circ$ . Addition of bromine to the alkaline solution oxidises it to 2 : 2'-dinitrobenzophenone. Reduction by iron and acetic acid converts it into 2 : 2'-diaminobenzophenone and 2 : 2'-diaminodiphenylmethane.

2 : 2'-Diaminodiphenylmethane is easily soluble in alcohol, less so in ether or benzene, and only slightly so in water, from which it crystallises in leaflets. Its hydrochloride crystallises in needles.

2 : 2'-Diaminobenzophenone forms a *hydrobromide* which crystallises in white leaflets, becoming yellow on exposure to light, and a *hydrochloride* crystallising in white leaflets which rapidly become reddish. Both salts are insoluble in benzene or ether, and are decomposed by water or alcohol. With sulphuric acid, the base forms a *sulphate*,  $C_{13}H_{12}ON_2 \cdot H_2SO_4$ , which crystallises in short, yellow prisms, and a hydrogen *sulphate*,  $C_{13}H_{12}ON_2 \cdot 2H_2SO_4$ , which crystallises in slightly red needles. The *picrate*,  $C_{13}H_{12}ON_2 \cdot (C_6H_3O_7N_3)_2$ , forms orange-coloured needles, which are easily soluble in warm water or alcohol, and decompose at  $164$ — $165^\circ$ . The action of acetic anhydride on the base leads to the *diacetyl* derivative which crystallises from alcohol in yellow needles and from ethyl acetate in prisms melting at  $154^\circ$ , and a substance which melts at  $164$ — $166^\circ$ . The base yields yellow crystalline diazo-salts which form red to violet dyes with resorcinol and  $\beta$ -naphthol.

Reduction of 2:2'-diaminobenzophenone with amyl alcohol and sodium yields a *base* which crystallises in glistening, white leaflets and melts at 131—133°. It forms a *hydrochloride* crystallising in white needles, and an *acetyl* derivative which crystallises in white needles and melts at 197—198°.

Methylation of 2:2'-diaminobenzophenone yields a *tetramethyldiaminobenzophenone* which crystallises in golden prisms, melts at 117—118°, is easily soluble in alcohol, ether, or benzene, and is volatile with steam. The *hydrochloride* crystallises in delicate needles or compact crystals. The hydrogen sulphate,  $C_{17}H_{20}ON_2 \cdot 2H_2SO_4$ , is easily soluble in water and crystallises in slightly yellow needles. The *picrate* crystallises from water in light yellow leaflets, from benzene in needles, and decomposes at 160—162°. Reduction of the tetramethyl base by amyl alcohol and sodium results in the decomposition of the ketone with probable formation of dimethylaniline. G. Y.

[Phenanthrene Sulphonic Acids and Phenanthrols]. By ALFRED WERNER [with BERNH. LÖWENSTEIN, AD. WACK, TOBIAS FREY, MAX KUNZ, K. REKNER, ADOLF NEY, H. HEIL, ADOLF SCHERRER, H. SCHWABACHER, JOHANNES KUNZ, and A. GROB] (*Annalen*, 1902, 321, 248—357. Compare Abstr., 1901, i, 696).—Sulphonation of phenanthrene, either with the ordinary concentrated or the fuming acid, shows that the phenanthrene sulphonic acids containing their sulphonic radicles in positions 2 and 3 are the chief products at 120—130°, whilst at 95—100° a good yield of phenanthrene-10-sulphonic acid is obtained. At temperatures above 140°, the amount of hydrocarbon destroyed becomes very large, and only a little of the 3-sulphonic acid is produced.

*Potassium phenanthrene-3-sulphonate*,  $C_{14}H_9SO_3K$ , crystallises in nacreous leaflets, the *barium* salt,  $Ba(C_{14}H_9SO_3)_2 \cdot 2\frac{1}{2}H_2O$ , is a pale yellow, granular powder. The free *sulphonic acid* separates in yellow, felted needles; the *chloride* crystallises from glacial acetic acid in pale yellow needles melting at 108·5°, and the *anilide*,  $C_{14}H_9 \cdot SO_2 \cdot NHPh$ , from dilute alcohol in lustrous white needles melting at 161°. The *methyl ester*, produced by the action of dimethyl sulphate on the potassium salt, melts at 119—120°.

*Potassium phenanthrene-10-sulphonate* crystallises in anhydrous, hexagonal plates, and yields phenanthraquinone on treatment with chromic acid, the *barium* salt crystallises in needles with  $2\frac{1}{2}H_2O$ . The *sulphonic acid* separates from very concentrated solutions in lustrous white needles; the *chloride* crystallises in stellar aggregates of needles melting at 125·5°; and the *anilide*,  $C_{14}H_9SO_2 \cdot NHPh$ , separates in prismatic crystals and melts at 165°.

*Ammonium phenanthrene-2-sulphonate*, obtained by boiling the crystallised ferrous salt with excess of ammonia, separates in white leaflets; it is reconverted into phenanthrene by heating with concentrated hydrochloric acid at 250°. The *potassium* salt, prepared by boiling the preceding compound with potassium hydroxide solution until all the ammonia is removed, crystallises in white leaflets. The *methyl ester*,  $C_{14}H_9 \cdot SO_3Me$ , obtained by the action of methyl sulphate

on the potassium salt, crystallises in white leaflets melting at 96—98° and having a blue fluorescence. The free sulphonic acid is not crystallisable.

3-Phenanthrol, obtained by fusing the corresponding potassium sulphonate with potassium hydroxide, melts at 122—123° and yields a *picrate* and a methyl ether melting respectively at 159° and 60—61° (compare Pschorr, Abstr., 1900, i, 233, 488).

*Nitro-3-phenanthryl methyl ether*,  $\text{NO}_2 \cdot \text{C}_{14}\text{H}_8 \cdot \text{OMe}$ , produced from the methyl ether by the action of nitric acid in glacial acetic acid solution, crystallises from alcohol in yellow needles and melts at 136·5—137°; on reduction with tin and hydrochloric acid, it yields *amino-3-phenanthryl methyl ether*,  $\text{NH}_2 \cdot \text{C}_{14}\text{H}_8 \cdot \text{OMe}$ , a substance crystallising in brown needles melting at 117—118° and yielding an insoluble hydrochloride which gives rise to an azo-compound on treatment with nitrite, and an alkaline solution of  $\beta$ -naphtholdisulphonic acid G. It was not, however, found possible to replace the amino-group by hydroxyl or chlorine.

*Acetylamino-3-phenanthryl methyl ether*,  $\text{OMe} \cdot \text{C}_{14}\text{H}_8 \cdot \text{NHAc}$ , obtained by heating the amine with acetic anhydride, crystallises in white leaflets, melts at 150°, and on oxidation with chromic acid furnishes a methoxyphenanthraquinone melting at 204°, this result indicating that the amino-group is situated in position 9 or 10.

*3-Phenanthryl ethyl ether*,  $\text{C}_{14}\text{H}_9 \cdot \text{OEt}$ , prepared by the action of ethyl iodide and sodium ethoxide on an alcoholic solution of 3-phenanthrol, separates in white crystals and melts at 46°; it may also be produced by means of diethyl sulphate. The ether is readily nitrated, yielding a *nitro-compound* crystallising in yellow needles and melting at 109—110°.

*3-Phenanthryl benzyl ether*,  $\text{C}_{14}\text{H}_9 \cdot \text{O} \cdot \text{C}_7\text{H}_7$ , obtained by the interaction of 3-phenanthrol, benzyl chloride, and sodium ethoxide, crystallises in lustrous leaflets, melts at 91—93°, and is readily soluble in the usual organic solvents.

*3-Phenanthroxycetic acid*,  $\text{C}_{14}\text{H}_9 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , results from the action of chloroacetic acid on an alkaline solution of 3-phenanthrol, and crystallises from ether in white, silky needles melting at 189—191°.

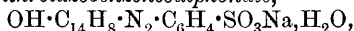
*3-Phenanthryl acetate*,  $\text{C}_{14}\text{H}_9 \cdot \text{OAc}$ , produced by heating the phenol with acetic anhydride at 120—130°, crystallises from alcohol in white plates and melts at 115—116°.

*3-Phenanthryl benzoate*,  $\text{C}_{14}\text{H}_9 \cdot \text{OBz}$ , which is prepared by adding benzoyl chloride to a pyridine solution of phenanthrol, crystallises from dilute alcohol in needles melting at 119°.

*3-Phenanthryl benzenesulphonate*,  $\text{C}_{14}\text{H}_9 \cdot \text{O} \cdot \text{SO}_2\text{Ph}$ , obtained by the Schotten-Baumann reaction, crystallises from methyl alcohol in stellar aggregates of prisms melting at 105—107°.

*Tri-3-phenanthryl phosphate*,  $\text{PO}(\text{O} \cdot \text{C}_{14}\text{H}_9)_3$ , produced by treating a strongly alkaline solution of 3-phenanthrol with phosphorus oxychloride, crystallises from toluene in small leaflets melting at 180—182°.

*Sodium 3-phenanthrolazobenzenesulphonate*,



is precipitated by adding hydrochloric acid to an alkaline solution of 3-phenanthrol and diazobenzenesulphonic acid; it crystallises from



dilute alcohol in lustrous red needles and dyes silk with a cherry-red colour.

*Amino-3-phenanthrol* results from the reduction of the preceding azo-compound with tin and hydrochloric acid, and crystallises from dilute alcohol in lustrous white needles melting at 159—161°. On treatment with nitrous acid, it yields a yellow compound which becomes resinous on warming. *Amino-3-phenanthrol hydrochloride* is most readily obtained by passing hydrogen chloride into an ethereal solution of the base; in hot aqueous solutions, oxidation occurs with the formation of a blue, soluble substance. *Diacetylamino-3-phenanthryl acetate*, the ultimate product of the action of acetic anhydride on the preceding amine, crystallises in sparingly soluble needles melting at 169—170°.

10-Phenanthrol (phenanthrone), produced by subjecting potassium phenanthrene-10-sulphonate to fusion with potash at 280—290°, crystallises from petroleum in lustrous pink needles melting at 152° (compare Abstr., 1883, 666; 1884, 81); the *picrate* crystallises from absolute alcohol in red needles melting at 183°.

10-Phenanthryl acetate forms needles melting at 77°; 10-*phenanthryl propionate*, obtained by the interaction of 10-phenanthrol and propionic anhydride at 180°, crystallises from glacial acetic acid in white needles melting at 95°. These compounds show that 10-phenanthrol (phenanthrone) is really a phenol and not a ketodihydrophenanthrene. 10-*Phenanthryl benzoate* and 10-*phenanthryl benzenesulphonate*,  $C_{14}H_9 \cdot O \cdot SO_2Ph$ , crystallise from dilute alcohol in white needles melting respectively at 96.7° and 88.5°; the former is obtained by mixing the phenol with benzoyl chloride in pyridine solution, the latter is produced by the Schotten-Baumann reaction.

*Benzenediazo-10-phenanthrol*,  $N_2Ph \cdot C_{14}H_9 \cdot OH$ , prepared by coupling benzenediazonium chloride and 10-phenanthrol in alkaline solution, crystallises from glacial acetic acid in deep red leaflets with a green reflex; it melts at 162—163°, and is identical with phenanthraquinone hydrazone (Zincke, *Ber.*, 1883, 16, 1564).

2-*Phenanthrol*, resulting from the fusion with potash of the ammonium or potassium salt of phenanthrene-2-sulphonic acid, crystallises from petroleum in lustrous, white leaflets and melts at 169°.

2-*Phenanthryl methyl ether*,  $C_{14}H_9 \cdot OMe$ , produced either by adding methyl iodide to sodium 2-phenanthroxide in absolute alcohol or by mixing an alkaline solution of the phenol with methyl sulphate, crystallises from glacial acetic acid in white leaflets melting at 100—101°; its *nitro*-derivative, obtained by nitration in glacial acetic acid, crystallises from this solvent in greenish-yellow leaflets melting at 190—191°.

2-*Phenanthryl acetate* crystallises from the ordinary organic solvents in white needles and melts at 142—143°.

2-*Phenanthryl benzoate*, produced by mixing its generators in pyridine solution, is obtained in white leaflets and melts at 139—140°.

2-*Phenanthrolazobenzenesulphonic acid*,  $SO_3H \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_8 \cdot OH$ , prepared by coupling the phenol with diazobenzenesulphonic acid in alkaline solution, is an amorphous, red substance dyeing yellow shades on silk.

A comparison of the properties of the preceding phenanthrols with those of the hydroxyphenanthrenes obtained by earlier investigators,

shows that Siemienski and also Rehs (Abstr., 1878, 76) were dealing with mixtures of the three isomerides; the phenanthrol described as melting at  $112^{\circ}$  is not a simple substance.

3-Phenanthrylamine, produced by heating the corresponding phenol with ammonia and ammonium chloride, exists in two modifications melting at  $143^{\circ}$  and  $87.5^{\circ}$  (compare Kunz, Abstr., 1901, i, 696); the modification of higher melting point changes into the more fusible variety on keeping for four months, and appears to be a labile poly-meride. Both varieties yield the same acetyl derivative melting at  $200-201^{\circ}$ .

*Benzoyl-10-phenanthrylamine* crystallises from xylene in white, silky needles melting at  $211^{\circ}$ ; the *phenylcarbamide* is a white, amorphous substance not melting below  $290^{\circ}$ ; the *urethane* derivative,  $C_{14}H_9 \cdot NH \cdot CO_2Et$ , crystallises in silky needles and melts at  $123^{\circ}$ .

2-Phenanthrylamine yields *benzoyl* and *urethane* derivatives crystallising in white needles and melting at  $216.5^{\circ}$  and  $125^{\circ}$ ; the *phenylcarbamide* is amorphous and decomposes at  $276^{\circ}$ .

*Phenyl-2-phenanthrylamine*, produced by heating the corresponding phenanthrol with aniline and calcium chloride, separates from light petroleum in hard, greenish crystals.

Potassium 3-phenanthrenesulphonate, when heated with anhydrous potassium ferrocyanide, yields *3-phenanthryl cyanide* crystallising from alcohol in white needles melting at  $102^{\circ}$ ; the product, on hydrolysis with potassium hydroxide in methyl alcohol, gives rise first to *3-phenanthramide*,  $C_{14}H_9 \cdot CO \cdot NH_2$ , and finally, after 55 hours, to 3-phenanthroic acid; the amide and acid crystallise in lustrous flakes melting at  $227-228^{\circ}$  and  $269^{\circ}$  respectively. This acid is identical with the substance obtained by Anschütz and by Japp.

10-*Phenanthryl cyanide*, produced by heating a mixture of the corresponding sulphonate and excess of potassium ferrocyanide, crystallises from alcohol in slender needles melting at  $103^{\circ}$ , and readily yields its amide and carboxylic acid on hydrolysis with potassium hydroxide dissolved in methyl alcohol. 10-*Phenanthramide* separates from water in white crystals melting at  $226^{\circ}$ ; 10-phenanthroic acid crystallises in yellowish-white needles melting at  $250^{\circ}$ , and is identical with Japp's  $\beta$ -phenanthrenecarboxylic acid (Trans., 1880, 37, 84). 2-*Phenanthryl cyanide*,  $C_{14}H_9 \cdot CN$ , crystallises from a mixture of benzene and petroleum and melts at  $105^{\circ}$ . 2-*Phenanthroic acid*,  $C_{14}H_9 \cdot CO_2H$ , obtained by alkaline hydrolysis in methyl alcohol solution, crystallises from glacial acetic acid in white needles melting at  $254^{\circ}$ .

The dibromophenanthrene, prepared from 10-bromophenanthrene, when quite pure, crystallises in needles, sinters at  $100^{\circ}$ , and melts at  $112-113^{\circ}$ . Dinitrophenanthraquinone, formerly obtained by Anschütz (Ber., 1876, 9, 1404) is readily produced by the use of fuming nitric acid, and when crystallised from glacial acetic acid melts at  $301-303^{\circ}$ .

2-*Nitrophenanthraquinone* results from the action of the concentrated acid of sp. gr. 1.4.

3-*Nitrophenanthraquinone*, prepared by the action of fuming nitric acid on 10-bromophenanthrene, crystallises in orange-coloured

needles and melts at 275°. On reduction with tin and hydrochloric acid, these nitroanthraquinones yield the corresponding aminophenanthraquinones; 3-aminophenanthraquinone crystallises from alcohol in brownish-red needles and melts at 254°; these amines are readily diazotised, and give rise to the corresponding hydroxyphenanthraquinones.

*Potassium 3-phenanthraquinonesulphonate*,  $C_{14}H_7O_2 \cdot SO_3K$ , produced by oxidising the corresponding phenanthrenesulphonate with chromic anhydride in glacial acetic acid, crystallises from dilute alcohol in lustrous, orange-yellow, felted needles, and is very soluble in water. The *barium* salt,  $(C_{14}H_7O_2 \cdot SO_3)_2Ba, 2\frac{1}{2}H_2O$ , is an orange-red precipitate sparingly soluble in water.

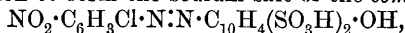
A compound giving the reactions of an oxime is obtained by condensing the sulphonate with hydroxylamine, but was not isolated in a state of purity. When treated with a 50 per cent. solution of potassium hydroxide, the phenanthraquinonesulphonate decomposes, yielding diphenylene ketone and 3-phenanthrol; this result is due to simultaneous oxidation and reduction. The tendency to revert to the parent hydrocarbon is also exhibited by the sulphonate on heating under pressure with concentrated hydrochloric acid. In this case, simultaneous reduction and hydrolysis result in the formation of phenanthrene. Fusion of the quinonesulphonate with potash leads to the production of 3-phenanthrol.

*Potassium diphenylenequinoxalinesulphonate*,  $C_6H_4 \begin{matrix} < N:C \cdot C_6H_4 \\ N:C \cdot C_6H_4 > \end{matrix} SO_3K$ , results from the condensation of the quinonesulphonic acid with *o*-phenylenediamine, and separates from water in an amorphous condition.

*Methyl 3-phenanthraquinonesulphonate*, produced by oxidising the corresponding alkyl phenanthrenesulphonate, is an orange-yellow, crystalline substance melting at 235°. 3-Phenanthraquinone cyanide,  $C_{14}H_7O_2 \cdot CN$ , resulting from the oxidation of 3-phenanthryl cyanide, crystallises from glacial acetic acid in orange-coloured leaflets melting at 282—283°; the corresponding *amide* is produced by oxidising 3-phenanthramide, and crystallises in orange-red needles, melting at 289—290°. 3-Phenanthraquinonecarboxylic acid, prepared by oxidising 3-phenanthroic acid, separates in reddish-yellow crystals and melts at 310°; it has already been obtained by Schultz (*Annalen*, 1879, 196, 14). 2-Phenanthraquinone cyanide,  $C_{14}H_7O_2 \cdot CN$ , produced from 2-phenanthryl cyanide, crystallises from glacial acetic acid in reddish-yellow leaflets and melts at 290°. 2-Phenanthraquinonecarboxylic acid,  $C_{14}H_7O_2 \cdot CO_2H$ , prepared by oxidising 2-phenanthroic acid, crystallises in reddish-yellow needles and melts above 300°. G. T. M.

*o*-Chloro-*p*-nitroaniline. By PAUL COHN (*Chem. Centr.*, 1902, i, 752; from *Mitt. Technol. Gewerb.-Mus. Wien* [ii], 11, 205—213. Compare Abstr., 1901, i, 407).—*o*-Chloro-*p*-nitroaniline, prepared from *p*-nitroaniline by Cassella & Co.'s method (*Patentbl.*, 21, 523), crystallises from water in slender, yellow needles, melts at 105°, is slightly soluble in cold water, completely so in a large volume of hot water, and readily so in hot alcohol or ether, but insoluble in light petroleum.

The *hydrochloride* crystallises from solutions strongly acidified with hydrochloric acid in four-sided plates, and is decomposed by water. The sulphate, oxalate, and picrate are very unstable. The *acetyl* derivative,  $C_8H_7O_3N_2Cl$ , crystallises from alcohol in faintly brownish-yellow crystals and melts at  $138-139^\circ$ . The *benzoyl* derivative,  $C_{13}H_9O_3N_2Cl$ , crystallises in pale yellow needles and melts at  $161^\circ$ . The azo-derivatives of chloro-*p*-nitroaniline have a bluer tinge than those of *p*-nitroaniline itself, and are not so readily attacked by acids or by light. Chloro-*p*-nitroaniline may be converted into 3:4-dichloro-1-nitrobenzene by Sandmeyer's reaction and when the diazo-compound is boiled with water it yields 2-chloro-4-nitrophenol. The diazo-compound combines with  $\beta$ -naphtholdisulphonic acid-G., in sodium carbonate solution to form the sodium salt of the compound



which separates as a scarlet precipitate; it dissolves on warming and on cooling crystallises in lustrous orange-red needles. The free *acid* crystallises in scarlet-red needles which have a silky lustre.

*Chloro-p-phenylenediamine*, obtained by reducing *o*-chloro-*p*-nitroaniline with tin and hydrochloric acid, crystallises from benzene or light petroleum in white needles and melts at  $63-64^\circ$ ; the *hydrochloride* crystallises in colourless needles. The sulphate, nitrate, oxalate, and picrate were also prepared. The *diacetyl* derivative crystallises in white needles, melts at  $197^\circ$ , and is readily soluble in alcohol but only very slightly so in benzene. The *dibenzoyl* derivative crystallises from chloroform in white needles and melts at  $228^\circ$ . Chloro-*p*-phenylenediamine, when warmed with hydrogen sulphide and ferric chloride, yields a violet-red chlorothiazine; with aniline and potassium dichromate, it forms a greenish-blue chloroindamine, and by oxidation with phenol in alkaline solution the corresponding chloroindophenol is obtained. By the action of potassium dichromate and sulphuric acid, chloro-*p*-phenylenediamine is converted into monochloroquinone, and with concentrated hydrochloric acid and bleaching powder it yields *monochloroquinone dichlorodi-imide*,  $C_6H_3Cl(NCl)_2$ , which crystallises from dilute alcohol in brownish-yellow needles, has a disagreeable odour resembling that of quinone, and melts at  $83-84^\circ$ . This compound reacts with acetic acid and resorcinol to form a dark violet dye.

E. W. W

**Pentanitro-1-nitromethylaminobenzene and Tetra- and Pentanitrophenol.** By J. J. BLANKSMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 4, 437-442).—By the action of concentrated nitric acid on *m*-nitromethylaniline and on 3:5-dinitromethylaniline, 2:3:4:6-tetranitro-1-nitromethylaminobenzene, and *pentanitro-1-nitromethylaminobenzene*,  $C_6(NO_2)_5 \cdot NMe \cdot NO_2$ , have respectively been obtained. The former has previously been prepared by van Romburgh (*Abstr.* 1889, i, 1154) from 2:4:5-trinitrodimethylaniline; the latter is a yellow, crystalline substance melting at  $132^\circ$ , and exploding at a higher temperature. When nitrated with a cold mixture of nitric and sulphuric acids, *m*-nitrophenol yields 2:3:4:6-tetranitrophenol, melting at  $140^\circ$ , and 3:5-dinitrophenol yields *pentanitrophenol*, which melts at  $190^\circ$ . If hot nitric acid is employed as the nitrating agent, 2:4:6-

trinitroresorcinol and trinitrophloroglucinol are respectively formed, as under these conditions a nitro-group which is flanked by two other nitro-groups is replaced by hydroxyl. Such a nitro-group can similarly be readily replaced by a methoxyl, ethoxyl, amino-, or phenylamino-group.

K. J. P. O.

**Anilnocitraconanil and its Derivatives.** By FRITZ FICHTER and ERNST PREISWERK (*Ber.*, 1902, 35, 1626—1630).—Citraconanil

forms with bromine an additive *product*,  $\begin{array}{c} \text{CBrMe}\cdot\text{CO} \\ | \\ \text{CHBr}\cdot\text{CO} \end{array} > \text{NPh}$ , which

crystallises in thick plates melting at 126—127°; by treatment with aniline in ethereal solution, it is converted into bromocitraconanil (m. p. 144·5—145·5°), but when heated with excess of aniline, anilino-citraconanil (m. p. 157°) is obtained. On reduction of the last-mentioned substance with aluminium amalgam, two stereoisomeric *α-anilino-*

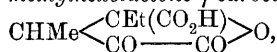
*methylsuccinanils*,  $\text{NHPh}\cdot\text{CH} < \begin{array}{c} \text{CHMe}\cdot\text{CO} \\ | \\ \text{CO}\text{---}\text{NPh} \end{array}$ , are formed; one crystal-

lises in white needles melting at 186·5—187°, the other in aggregates of needles melting at 134°. On hydrolysing anilnocitraconanil with

sulphuric acid, *methylloxalacetanil*,  $\begin{array}{c} \text{CHMe}\cdot\text{CO} \\ | \\ \text{CO}\text{---}\text{CO} \end{array} > \text{NPh}$ , is obtained as

colourless needles decomposing at 196°; it forms a yellow solution in water or alcohol which gives a dark brown coloration with ferric chloride, and its salts are yellow in colour and yield yellow solutions; the enolic form of this compound would thus appear to have a yellow colour. The *phenylhydrazone* crystallises in yellow, flattened needles melting at 183—184°. *Bromomethylloxalacetanil* forms pale yellow needles melting at 134°.

By prolonged treatment of anilnocitraconanil with concentrated sulphuric acid, *α-keto-β-methylhexolactone-γ-carboxylic acid*,



is obtained, probably being produced by condensation of the propionyl-formic acid first formed; it forms crystals melting at 128° and gives a violet coloration with ferric chloride.

K. J. P. O.

**Methylation of 6-Nitro-*o*-toluidine.** By ALEXANDER VON TATSCHALOFF (*J. pr. Chem.*, 1902, [ii], 65, 239—242).—The *hydrobromide* of 6-nitro-*o*-toluidine crystallises in clusters of yellowish leaflets or long, thin needles and is decomposed when treated with water. The *hydriodide* crystallises in rhombohedra or flat prisms. The hydrobromide, when heated with methyl alcohol for 6—10 hours at 100—110°, yields a mixture of 6-nitro-*o*-dimethyltoluidine and its *hydrobromide*; the base boils at 191—192° under 9·5—10 cm. pressure and solidifies in the cold to a mass of transparent golden crystals melting at 25—25·5°; the hydrobromide crystallises in bright greyish-brown leaflets.

R. H. P.

**Methylation of 5-Nitro-*m*-toluidine.** By AD. HAIBACH (*J. pr. Chem.*, 1902, [ii], 65, 242—246. Compare preceding abstract).—The *hydrobromide* of 5-nitro-*m*-toluidine crystallises in thin leaflets.

5-Nitro-m-dimethyltoluidine crystallises from ether in dark red, flat, rhombic pyramids and melts at 48—50°. 5-Nitro-m-tolyltrimethylammonium bromide crystallises, with 2H<sub>2</sub>O, in large, rhombic prisms, and, when treated with moist silver oxide, yields trimethylamine and s-nitrocresol. R. H. P.

Methylation of 2-Nitro-p-toluidine. By AD. HAIBACH (*J. pr. Chem.*, 1902, [ii], 65, 246—248. Compare preceding abstracts).—The hydrobromide of 2-nitro-p-toluidine crystallises in large laminae. 2-Nitro-p-dimethyltoluidine was obtained as a reddish, crystalline mass melting at 35°, and 2-nitro-p-tolyltrimethylammonium bromide crystallises, with  $\frac{1}{2}$ H<sub>2</sub>O, in colourless, rhombic prisms or pyramids. R. H. P.

Methylation of 4-Nitro-o-toluidine. By O. STADEN (*J. pr. Chem.*, 1902, [ii], 65, 249—252. Compare preceding abstracts).—The hydrobromide of 4-nitro-o-toluidine was obtained in the form of small, lustrous, pale red crystals, 4-nitro-o-dimethyltoluidine in golden leaflets or rods melting at 14°, and 4-nitro-o-tolyltrimethylammonium bromide in small, colourless, tabular crystals. R. H. P.

Formation of Quaternary Aromatic Bases. By S. SCHLIOM (*J. pr. Chem.*, 1902, [ii], 65, 252—257. Compare preceding abstracts).—Comparative experiments show that quaternary aromatic bases are more readily formed by compounds with a side chain in the meta- or para-position to the amino-group than by those with a side chain in the ortho-position. R. H. P.

Molecular Rearrangement of Unsymmetrical Acylthiocarbamides and Acyl-ψ-thiocarbamides into the Isomeric Symmetrical Derivatives. By HENRY L. WHEELER (*Amer. Chem. J.*, 1902, 27, 270—280).—When phenyl-ψ-methylthiocarbamide, NH<sub>2</sub>·C(SMe)·NPh, dissolved in dry ether, is treated at 0° with acetyl chloride, it is converted partly into an acetyl derivative and partly into the hydrochloride. The former crystallises from ether in colourless prisms melting at 85—86° and is decomposed in the cold by alkalis with the formation of methyl thiocyanate and acetanilide and has therefore the constitution NH<sub>2</sub>·C(SMe)·NPh·COMe. It combines with hydrogen iodide to form a hydriodide, insoluble in ether, crystallising from hot alcohol in the form of colourless four- and six-sided plates and melting at 152°. The latter is also formed by the addition of methyl iodide to the labile acetylphenylthiocarbamide obtained by Hegershoff (*Abstr.*, 1900, i, 156), which must therefore be represented by the formula NH<sub>2</sub>·CS·NPhAc instead of NHPH·CS·NHAc, as proposed by the latter author. The transformation of these unsymmetrical thiocarbamides into their symmetrical isomerides may be represented as taking place in one of the two following ways: NH<sub>2</sub>·CS·NPhAc → NHAc·CS·NHPH or NH<sub>2</sub>·C(SH)·NPhAc → NHAc·C(SH)·NPh. T. A. H.

Removal of Sulphur from Aryldithiocarbamates. By GUSTAVE HELLER and WILHELM BAUER (*J. pr. Chem.*, 1902, [ii], 65, 365—386).—Monoaryldithiocarbamides are obtained by the action of lead carbonate (1 mol.) on the corresponding ammonium aryldithio-

carbamates; by the action of lead carbonate (2 mols.) in the presence of alkali (1 mol.), arylcyanamides are formed.

The following new compounds are described:

*p*-Tolylcyanamide crystallises in prisms, melts at 69°, and is easily soluble in alcohol, ether, chloroform, or benzene. Its silver derivative,  $C_8H_7N_2Ag$ , crystallises in leaflets; the *platinichloride* forms orange-red prisms which decompose at about 155°. The *benzoyl* derivative melts at 126°. *p*-Tolylcyanamide and glycine condense to form glycolmono-*p*-tolylguanidine,  $C_{10}H_{13}O_2N_3$ , which is soluble in dilute hydrochloric acid, becomes brown at 240°, and melts with evolution of gas at 262°. When heated in benzene solution, *p*-tolylcyanamide polymerises to *tri-p-tolylisomelamine*, which crystallises with benzene in needles,  $C_{24}H_{24}N_6$ ,  $C_6H_6$ , melting at 183°. It is easily soluble in ether, alcohol, or hydrochloric acid. The crystals lose  $C_6H_6$  at 135–140°. It yields a *triacetyl* derivative which forms colourless crystals, becoming slightly yellow at 205° and melting with decomposition at 236°.

*m*-Tolylcyanamide forms crystals which melt at the ordinary temperature. Its *benzoyl* derivative melts at 69°.

$\beta$ -Naphthylcyanamide crystallises in colourless leaflets, melts at 102° and is easily soluble in alcohol, ether, or chloroform.

*p*-Ethoxyphenylthiocarbamide is found to melt at 172° and *p*-ethoxyphenylcyanamide at 87° (compare Abstr., 1885, 148). When recrystallised from benzene, the cyanamide yields a substance, probably a *polymeride*, melting at 170°.

When boiled with water, ammonium phenyldithiocarbazinate yields diphenylthiosemicarbazide (m. p. 176°), hydrogen sulphide, ammonia, phenylhydrazine, and a yellow substance which melts at 80–85°.

*Phenyl-o-tolylguanidine* formed from *o*-tolylcyanamide and aniline hydrochloride, or from phenylcyanamide and *o*-toluidine hydrochloride, melts at 123–125°. *o-p-Ditolylguanidine* melts at 120–121°. *Phenyl-p-tolylguanidine* melts at 120–122°. G. Y.

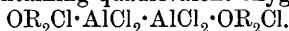
**Acetyl Compounds of Benzenoid and Naphthalenoid Aminosulphonic Acids.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 129000).—The neutral salts of the aromatic aminosulphonic acids, when suspended or dissolved in water at the ordinary temperature or at 50°, can be readily acetylated by the addition of acetic anhydride. The acetyl derivatives of sulphanilic, metanilic, *o*- and *p*-toluidinesulphonic, and *o*, *m*-, and *p*-aminobenzoic acids have been obtained in this way and the reaction is equally applicable to the sulphonic acids of  $\alpha$ - and  $\beta$ -naphthylamine. The salts of *m*- and *p*-phenylenediaminesulphonic and *m*-tolylenediaminesulphonic acids yield the *mono*- or *di-acetyl* derivatives, according to the amount of acetic anhydride employed. G. T. M.

**Preparation of Oxyamidines.** By HEINRICH LEY (*Ber.*, 1902, 35, 1451–1453).—Oxyamidines can be advantageously prepared by the action of  $\beta$ -substituted hydroxylamines on imino-ethers. From phenylhydroxylamine and methylisoformanilide,  $OMe \cdot CH : NPh$ , Bamberger and Tschirner's diphenyloxyformamidine (this vol., i, 276) was obtained, whilst *p*-tolylhydroxylamine gave 1-phenyl-3-*p*-tolylloxyform-

*amidine*, of which the *copper* salt only was isolated; this crystallises from toluene and melts at 248°.

T. M. L.

**Structure of the Substances obtained by the Addition of Organic Oxygen Compounds and Aluminium Haloids.** By ELMER P. KOHLER (*Amer. Chem. J.*, 1902, 27, 241—257).—When an aluminium haloid is mixed with an oxygenated carbon compound, dissolved in a suitable solvent, for example, carbon disulphide, an additive product is formed containing 1 mol. of the aluminium salt with 2 mols. of the substance, if the latter contains one atom of oxygen, or with 1 mol. if it contains two oxygen atoms: thus aluminium bromide combines with anthraquinone to form the derivative  $\text{Al}_2\text{Br}_6\cdot\text{C}_{14}\text{H}_8\text{O}_2$ , and with phenyl ether to produce the compound  $\text{Al}_2\text{Br}_6\cdot 2(\text{C}_6\text{H}_5)_2\text{O}$ . Similar additive products of anisole, terephthalyl chloride, methylene, phenylene ether, acetophenone, acetylmesitylene and its chloro- and dichloro-derivatives, dibenzylideneacetone, xanthone, acetylacetone, and chloroacetyl chloride have been isolated. These substances usually crystallise well, dissolve in carbon disulphide, and decompose when heated. The observations of the author are not in accord with the formulæ proposed by Gustavson (*Abstr.*, 1888, 575) and by Kronberg (*Abstr.*, 1900, i, 502) for compounds of this type, and he proposes to represent them as containing quadrivalent oxygen thus:



T. A. H.

**Sitosterol.** By E. RITTER (*Zeit. physiol. Chem.*, 1902, 34, 461—480. Compare Burian, *Abstr.*, 1898, i, 72).—Sitosterol, after six crystallisations from alcohol, melts at 136·5°. In ethereal solution, it gives  $[\alpha]_D - 26\cdot40^\circ$  and in chloroform solution  $-33\cdot91^\circ$ . Analyses agree best with one or other of the formulæ  $\text{C}_{26}\text{H}_{43}\cdot\text{OH}\cdot\text{H}_2\text{O}$ ,  $\text{C}_{27}\text{H}_{45}\cdot\text{OH}\cdot\text{H}_2\text{O}$ .

The alcoholic mother liquors yield a second crystalline modification of sitosterol in the form of flat needles.

The following esters have been prepared, namely: Benzoate melting at 145·5; *cinnamate* melting at 158° and exhibiting strong fluorescence; *palmitate* from sitosterol and palmitic acid, glistening flakes melting at 90°; *stearate* melting at 89—90° to a turbid liquid which clarifies at 118—119°; *oleate*, colourless needles melting at 35·5°. Boiling alcoholic potash is practically without action on sitosterol.

J. J. S.

**Bufonin and Bufotalin, the Active Components of the Secretions of the Skin Glands of the Toad.** By EDWIN S. FAUST (*Chem. Centr.*, 1902, i, 891—892; from *Arch. exp. Path. Pharm.*, 47, 278—310).—*Bufonin*,  $(\text{C}_{17}\text{H}_{26}\cdot\text{OH})_2$ , obtained by extracting the skins of toads with 96 per cent. alcohol, crystallises from alcohol in slender needles or thicker prisms, melts at 152°, and is readily soluble in chloroform, benzene, or hot alcohol. With chloroform and with acetic anhydride and concentrated sulphuric acid, it gives reactions similar to those of cholesterol, but it does not give the cholesterol reaction with hydrochloric acid and ferric chloride, and is not attacked by boiling with alcoholic sodium hydroxide solution. *Bufonin chloride*, prepared by the action of phosphorus pentachloride on bufonin, crystallises from



hot alcohol in needles grouped together in feathery aggregates and melts at  $103^{\circ}$ . When the chloride is reduced with sodium ethoxide, a hydrocarbon (analogous to cholestene?) is obtained which forms an additive compound with bromine.

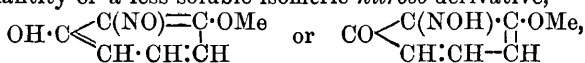
The alcoholic extract of the skin also contains an acid *bufotalin*,  $C_{34}H_{46}O_{10}$  which is probably an oxidation product of bufonin; it is very soluble in chloroform, alcohol, glacial acetic acid, acetone, or alkalis. Bufotalin is precipitated by tannin, or by phosphotungstic or phosphomolybdic acid.

When bufotalin is oxidised by chromic mixture, a product is obtained of which a portion is soluble in ammonia; on acidification, the ammoniacal solution gives a white, flocculent precipitate the physiological properties of which resemble those of bufotalin. Bufotalin is the active component of the secretion of the skin of the toad, and when injected subcutaneously, it has a physiological action similar to that of digitalin, diminishing the frequency of the pulse, but increasing its volume and the pressure of the blood in warm-blooded animals. When applied subcutaneously, it affects the intestines and respiratory organs, eventually causing death, but it has no action on the nervous system. Administration *per os* only causes local irritation, and very large doses are required to be fatal. Bufonin is less soluble than bufotalin and has consequently a weaker physiological action.

A cholesterol derivative possessing similar physiological properties has also been prepared.  
E. W. W.

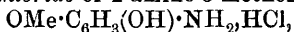
#### Action of Nitrous Acid on Resorcinol Monomethyl Ether.

By FERDINAND HENRICH and OTTO RHODIUS (*Ber.*, 1902, **35**, 1475—1486. Compare Abstr., 1896, i, 476, and 1900, i, 163).—The monomethyl ether of resorcinol (1 mol.) dissolved in a mixture of alcohol and acetic acid, was treated with a concentrated solution of sodium nitrite (1 mol.); the product, when dry, was extracted with cold benzene; the soluble material consists of (i) a small quantity of a very soluble *nitroso*-derivative,  $OH \cdot C \begin{smallmatrix} \swarrow CH:C(OMe) \\ \searrow C(NO)-CH \end{smallmatrix} > CH$  (?), which forms brownish crystal aggregates melting at  $138^{\circ}$ ; and (ii) a much larger quantity of a less soluble isomeric *nitroso*-derivative,



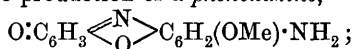
which exists in two modifications; the one forms green crystals, which become suddenly yellow at  $128$ — $130^{\circ}$  and melt at  $154^{\circ}$ , and is obtained when the compound is crystallised from benzene; the other form is obtained from alcoholic solutions of the *nitroso*-derivative, and crystallises in brownish-yellow needles melting at  $154^{\circ}$ . Both forms have mol. weights corresponding with the simple formula. The view is expressed that one form corresponds with an *o*-quinoneoxime, and the other to an *o*-nitrosophenol. The *potassium* salt,  $OMe \cdot C_6H_3(NO) \cdot OK$ , is obtained by mixing alcoholic solutions of potassium hydroxide and the *nitroso*-derivative.

On reduction with stannous chloride and hydrochloric acid, both forms yield the *hydrochloride* of 2-amino-3-methoxyphenol,



which forms crystals melting at  $214^{\circ}$ ; the base is very readily oxidised; the *picrate* forms yellowish-green crystals; the *triacetyl* derivative,  $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OAc}) \cdot \text{N} \cdot \text{Ac}_2$ , obtained when the hydrochloride is heated with acetic anhydride at  $140^{\circ}$ , crystallises in small cubes melting at  $92^{\circ}$ . When the last-mentioned substance is heated at  $200$ — $240^{\circ}$ , *2-methyl-4-methoxybenzoxazole*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \langle \text{N} \rangle \text{CMe}$ , distils over, and crystallises in large, white needles melting at  $57^{\circ}$ . On benzoylating the hydrochloride of the base by the Schotten-Baumann method, a *monobenzoyl* derivative is obtained melting at  $163^{\circ}$ ; when distilled, *4-methoxy-3-phenylbenzoxazole*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \langle \text{N} \rangle \text{CPh}$ , is formed, and crystallises in yellowish needles melting at  $65$ — $66^{\circ}$ .

An alkaline solution of 2-amino-3-methoxyphenol is rapidly oxidised by the air, with the production of a *phenoxazine*,

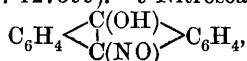


it crystallises in dark-red crystalline aggregates, which darken at  $260$ — $270^{\circ}$ , melt and decompose at  $300$ — $302^{\circ}$ , and dissolve in sulphuric acid with a violet coloration, becoming red on adding water; the *monoacetyl* derivative crystallises in brick-red needles. On reduction of the phenoxazine with zinc dust and acetic acid in the presence of acetic anhydride, a *substance*,  $\text{C}_{13}\text{H}_9\text{O}_3\text{N}_2(\text{OAc})_3$ , was obtained as colourless crystals.

*p-Nitroso-m-methoxyphenol*,  $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{NO}) \cdot \text{OH}$ , is left undissolved on extracting with cold benzene the product of the action of nitrous acid on resorcinol monomethyl ether; it crystallises in yellow leaflets, which begin to darken and decompose at  $160$ — $170^{\circ}$ ; on reduction, *p-amino-m-methoxyphenol hydrochloride* is obtained, crystallising in greyish-blue crystals. Oxidation of the latter produces methoxyquinone (m. p.  $140^{\circ}$ ).  
K. J. P. O.

*s-o-p-Dihydroxydiphenylmethane*. By VICTOR WAGNER (*J. pr. Chem.*, 1902, [ii], 65, 313—315).—*2:4'-Dihydroxydiphenylmethane*, obtained from 2:4'-diaminodiphenylmethane, crystallises from alcohol in delicate needles or straw-yellow, rhombic prisms, melts at  $117$ — $118^{\circ}$ , and is slightly soluble in water, easily in alcohol or ether. It yields a *dibenzoyl* derivative which forms silky needles melting at  $108^{\circ}$ , a *diacetyl* derivative which crystallises in delicate, glistening needles melting at  $70^{\circ}$ , a *diethyl* ether, which forms white needles melting at  $60^{\circ}$ , and a *dimethyl* ether which separates from methyl alcohol in colourless crystals which melt at  $26^{\circ}$ .  
G. Y.

*o-Nitroanthracene* [Nitrosoanthranol]. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 127399).—*9-Nitrosoanthranol*,



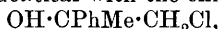
prepared by adding 60 per cent. nitric acid to a suspension of anthracene in glacial acetic acid, is precipitated from the clear yellow solution thus obtained in the form of anthracene nitrochloride by the addition of concentrated hydrochloric acid; this intermediate

product separates from benzene or toluene in white needles melting at  $163^{\circ}$ , and is converted into nitrosoanthranol by treatment with a solution of ammonia, sodium hydroxide, or the corresponding carbonate.

The yellow solution obtained by the action of nitric acid when poured into water and treated with alkaline solutions also yields nitrosoanthranol, and this substance is also obtained by adding concentrated sulphuric acid to the product of nitration dissolved either in glacial acetic acid or in nitrobenzene. G. T. M.

**Molecular Fission produced by Bromine.** By R. FOSSE (*Compt. rend.*, 1902, 134, 904—906. Compare Abstr., 1901, 322, 384, 604, 643, and this vol., i, 51, 171, 304).—The *eso*anhydride of 2:2':2''-tri-hydroxy-1:1':1''-trinaphthylmethane, when treated with bromine in bromoform or glacial acetic acid, undergoes disruption, a mol. of the substance yielding 1 mol. of 1-bromo- $\beta$ -naphthol and 1 mol. of dinaphthaxanthonium bromide. The original substance having been formed by the condensation of 2-hydroxy-1-naphthaldehyde and  $\beta$ -naphthol, this decomposition affords an indirect method of substituting bromine for the aldehydic complex. The fact that 1-bromo- $\beta$ -naphthol is the product of the fission is additional evidence in favour of the constitution assigned to 2-hydroxy-1-naphthaldehyde. G. T. M.

**Constitution of Chlorohydrins.** By MARC TIFFENEAU (*Compt., rend.*, 1902, 134, 774—775).—The action of hypochlorous acid on  $\beta$ -phenylmethylethylene ( $\beta$ -allylbenzene),  $\text{CPhMe}:\text{CH}_2$ , yields a chlorohydrin which has a sp. gr. 1.220 at  $0^{\circ}$ , boils at  $130$ — $132^{\circ}$  under 16 mm. pressure and is identical with the chlorohydrin,



obtained by the action of chloroacetone on magnesium phenyl bromide. The action of chloroacetone on magnesium methyl iodide yields the chlorohydrin,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\text{Cl}$ , and its action on magnesium ethyl bromide yields the chlorohydrin,  $\text{OH}\cdot\text{CMeEt}\cdot\text{CH}_2\text{Cl}$ , which boils at  $149$ — $151^{\circ}$ , and has a sp. gr. 1.053 at  $0^{\circ}$ . These results are regarded as supporting Krassusky's conclusion (Abstr., 1901, i, 246) that when hypochlorous acid combines with ethylenic hydrocarbons the hydroxyl group always attaches itself to the carbon atom combined with the smallest number of hydrogen atoms. C. H. B.

**Action of Methyl and Ethyl Alcohols on the Bromides of certain Propenyl Compounds.** By F. J. POND, E. S. ERB, and A. G. FORD (*J. Amer. Chem. Soc.*, 1902, 24, 327—346).—When a solution of anethole dibromide in methyl alcohol is boiled for an hour in a reflux apparatus, hydrogen bromide is eliminated and an *additive* compound,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OMe})\cdot\text{CHMeBr}$ , of bromoanethole with methyl alcohol is obtained as a pale yellow, mobile oil which dissolves readily in alcohol, ether, chloroform, or acetic acid, and is decomposed by heat. If this oil is treated with sodium methoxide or ethoxide and the product boiled with hydrochloric acid, anisyl ethyl ketone is obtained. By the action of ethyl alcohol on anethole dibromide, the *compound*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OEt})\cdot\text{CHBrMe}$ , is produced, and is converted by sodium ethoxide into anisyl ethyl ketone.

If bromoanethole dibromide is boiled with methyl alcohol, the compound,  $\text{OMe} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CH}(\text{OMe}) \cdot \text{CHMeBr}$ , is obtained which crystallises from acetone in large, colourless prisms, melts at  $71-74^\circ$ , and boils without decomposition at  $160-164^\circ$  under 14—15 mm. pressure; it does not decolorise permanganate solution or absorb bromine. By the action of sodium methoxide, it is converted into bromoanisyl ethyl ketone, first obtained by Hell and Hollenberg (Abstr., 1896, i, 354), which crystallises in long needles and melts at  $100-101^\circ$ ; the oxime melts at  $108^\circ$ . The corresponding additive compound with ethyl alcohol,  $\text{OMe} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CH}(\text{OEt}) \cdot \text{CHMeBr}$ , is a mobile, amber-coloured oil which is converted by sodium ethoxide into bromoanisyl ethyl ketone.

The compounds formed by the action of methyl and ethyl alcohols on isosafrole dibromide were obtained as oils which could not be purified. By the action of sodium ethoxide on the methyl alcohol compound, a liquid is produced which yields an oxime identical with that obtained by the action of sodium methoxide on isosafrole dibromide (Wallach and Pond, Abstr., 1896, i, 95).

The compound,  $\text{CH}_2\text{:O}_2 \cdot \text{C}_6\text{H}_2\text{Br} \cdot \text{CH}(\text{OMe}) \cdot \text{CHMeBr}$ , obtained by the action of methyl alcohol on bromoisosafrole dibromide, crystallises in needles or prisms, melts at  $75-76.5^\circ$ , and is not affected by sodium methoxide. The corresponding ethyl compound forms large, rhombohedral crystals, melts at  $58-60^\circ$ , and is not affected by sodium ethoxide.

The compound,  $\text{CH}_2\text{:O}_2 \cdot \text{C}_6\text{Br}(\text{OMe})_2 \cdot \text{CH}(\text{OMe}) \cdot \text{CHMeBr}$ , formed by the action of methyl alcohol on bromoisosafrole dibromide, crystallises in large prisms and melts at  $92^\circ$ . The corresponding compound with ethyl alcohol was obtained as a dark-coloured, viscous oil.

The compound,  $\text{OEt} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{CH}(\text{OMe}) \cdot \text{CHMeBr}$ , obtained by the action of methyl alcohol on ethylisoeugenol dibromide, crystallises from alcohol in colourless prisms and melts at  $68^\circ$ ; another compound is simultaneously produced which crystallises in slender needles, melts at  $128^\circ$ , and does not contain bromine. E. G.

**Hydrolysis of Glyceryl Tribenzoate.** By LUIGI BALBIANO (*Gazzetta*, 1902, 32, i, 265—279).—In confirmation of the views of Henriques (*Mon. Sci.*, 1898, [iv], 12, 717), the author has shown that 1 mol. of sodium alkoxide is sufficient to convert a glyceride such as glyceryl tribenzoate into glycerol according to the equation:  $\text{C}_3\text{H}_5(\text{OBz})_3 + \text{NaOEt} + \text{EtOH} + \text{H}_2\text{O} = \text{C}_3\text{H}_5(\text{OH})_3 + \text{C}_6\text{H}_5 \cdot \text{CO}_2\text{Na} + 2\text{C}_6\text{H}_5 \cdot \text{CO}_2\text{Et}$ . He further finds that the minimum proportion of sodium ethoxide necessary to bring about the complete hydrolysis of the tribenzoate by alcohol according to the equation:  $\text{C}_3\text{H}_5(\text{OBz})_3 + 3\text{EtOH} = \text{C}_3\text{H}_5(\text{OH})_3 + 3\text{C}_6\text{H}_5 \cdot \text{CO}_2\text{Et}$ , is 1/50 gram-mol.; the presence of water is not required to bring about this reaction, which does not proceed step by step through mono- and di-glycerides but yields at once glycerol.

The opposing views of Geitel (Abstr., 1897, ii, 547) and of Lewkowitsch (Proc., 1899, 190) are discussed, and the author considers the theory advanced by Beilstein and Kossel concerning the mechanism of the action of sodium ethoxide on glyceryl tribenzoate to be the most likely one. T. H. P.

**The Reaction between Acid Chlorides and Formaldehyde.** By MARCEL DESCUDÉ (*Compt. rend.*, 1902, 134, 1065—1067).—It has already been proved (this vol., i, 339) that chloromethyl benzoate is formed when formaldehyde reacts with benzoyl chloride in presence of zinc chloride:  $\text{—C}_6\text{H}_5\cdot\text{COCl} + \text{CH}_2\text{O} = \text{C}_6\text{H}_5\cdot\text{CO}_2\cdot\text{CH}_2\text{Cl}$ . Benzoic anhydride, dichloromethyl oxide, and methylene dibenzoate are also produced (compare Abstr., 1901, i, 357, 504). The reactions which take place are explained to be:  $2\text{C}_6\text{H}_5\cdot\text{CO}_2\cdot\text{CH}_2\text{Cl} = (\text{C}_6\text{H}_5\cdot\text{CO})_2\text{O} + (\text{CH}_2\text{Cl})_2\text{O}$  and  $(\text{C}_6\text{H}_5\cdot\text{CO})_2\text{O} + \text{CH}_2\text{O} = (\text{C}_6\text{H}_5\cdot\text{CO}_2)_2\text{CH}_2$ .

With phthalyl chloride, formaldehyde gives dichloromethyl phthalate, phthalic anhydride, and dichloromethyl oxide, but no methylene diphtalate. A similar reaction takes place with acetyl chloride.

J. MCC.

**2-Chloro-3-aminobenzoic Acid.** By ARNOLD F. HOLLEMAN [with G. L. VOERMAN] (*Rec. Trav. Chim.*, 1902, [ii], 21, 56—58. Compare Abstr., 1901, i, 638).—On saturating with hydrogen sulphide an ammoniacal solution of 2-chloro-3-nitrobenzoic acid (*loc. cit.*), 2-chloro-3-aminobenzoic acid is obtained. It melts at  $158^\circ$ , whereas Griess (*Ber.*, 1886, 19, 316) gives  $185^\circ$ , and has  $K$  0.066.

*m*-Aminobenzoic acid was prepared from *m*-nitrobenzoic acid by reduction with ammonium sulphide and subsequent precipitation of the acid with tartaric acid—a method which gives a better yield than that recommended by Gerland (*Annalen*, 1834, 19, 188). 2-Chloro-3-aminobenzoic acid could not be obtained from *m*-aminobenzoic acid by Griess's method.

K. J. F. O.

**Ethereal  $\omega$ -Cyanomethylantranilates.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 129375).— $\omega$ -Cyanomethylantranilic acid, when treated for a short time with mild esterifying agents, yields the corresponding esters without undergoing hydrolysis. Thus, methyl  $\omega$ -cyanomethylantranilate,  $\text{CN}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ , can be obtained by the action of methyl alcohol and sulphuric acid, and the ethyl ester by that of ethyl alcohol and hydrochloric acid on the acid.

G. T. M.

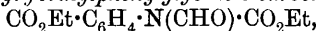
**Phenylglycine-*o*-carboxylic Acid.** DANIEL VORLÄNDER and RUDOLF VON SCHILLING (D.R.-P. 127577. Compare Abstr., 1901, i, 710).—Nitroso-*o*-tolylglycine, prepared by the action of nitrous acid on *o*-toluidinediacetic acid,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , is oxidised by permanganate to nitrosophenylglycine-*o*-carboxylic acid, and may thus be employed in the production of indigo (compare Vorländer, Abstr., 1901, i, 463).

G. T. M.

**N-Alkyl Derivatives of Phenylglycine-*o*-carboxylic Acid.** By DANIEL VORLÄNDER and ERICH MUMME (*Ber.*, 1902, 35, 1699—1701).—The N-alkyl derivatives of phenylglycinecarboxylic acid may be prepared by heating the aqueous solution of the sodium salt of the acid with an alkyl iodide. N-Methylphenylglycinecarboxylic acid melts and decomposes at about  $189^\circ$ . N-Ethylphenylglycinecarboxylic acid melts and decomposes at  $184$ — $186^\circ$ ; it has also been prepared from chloro-

acetic acid and ethylanthranilic acid. *N-Benzylphenylglycinecarboxylic acid* melts and decomposes at 190° after previously sintering. These acids are more strongly basic than phenylglycinecarboxylic acid itself, and show no characteristic reaction with fuming sulphuric acid. *Dimethyl N-methylphenylglycinecarboxylate*, prepared by direct esterification or by the action of dimethyl sulphate on phenylglycinecarboxylic acid or the *N*-methyl acid, melts at 82–83°. This substance, and the other normal esters of the *N*-alkylphenylglycinecarboxylic acids, are readily converted by alkalis and alkali carbonates into indoxyl derivatives. Methyl *N*-methylphenylglycinecarboxylate yields a mixture of two isomeric *methyl N-methylindoxylates*, one of which melts at 144–146°, and the other at about 88°. A. H.

**Acyl Derivatives of Diethyl Phenylglycine-*o*-carboxylates.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 127648. Compare Abstr., 1901, i, 710).—*Diethyl formylphenylglycine-*o*-carboxylate*,



produced by heating diethyl phenylglycine-*o*-carboxylate with 90 per cent. formic acid at 150°, is readily soluble in most organic solvents and crystallises with great difficulty; the dimethyl ester also yields a *formyl* derivative.

*Diethyl benzoylphenylglycine-*o*-carboxylate*,  $\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_4 \cdot \text{NBz} \cdot \text{CO}_2\text{Et}$ , obtained by the action of benzoyl chloride on the diethyl ester at 100°, is a viscid oil; the *benzoyl* derivative of the dimethyl ester is oily, but solidifies to a waxy mass on cooling.

*Triethyl phenylglycine-*o*-dicarboxylate*,  $\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{CO}_2\text{Et})_2$ , results from the action of ethyl chloroformate on diethyl phenylglycine-*o*-carboxylate at 100°; it melts at 48°, boils with decomposition above 360°, and rapidly dissolves in the usual organic solvents. The corresponding trimethyl ester is a viscid, yellow oil boiling at 210–215° under 10 mm. pressure. G. T. M.

***iso*Salicylic Acid.** By HEINRICH BRUNNER (*J. pr. Chem.*, 1902, [ii], 65, 304).—*isoSalicylic acid*,  $\begin{array}{c} \text{C}(\text{CO}_2\text{H}) \cdot \text{CH} \text{---} \text{CH} \\ \parallel \qquad \qquad \qquad \text{>O} \qquad \parallel \\ \text{CH} \text{---} \text{CH} \text{---} \text{CH} \end{array}$  (?), obtained

by the action of aqua regia on an alcoholic solution of salicylic acid, crystallises in prisms and melts at 154°, but sublimes at a much lower temperature. The alkali salts are yellow and are converted into salicylates by continued action of alkalis. The *dibromo*-derivative crystallises in lemon-coloured prisms, forms red alkali salts, and is converted into dibromosalicylic acid when reduced with nascent hydrogen. R. H. P.

**Oxidation of Anethole and Analogous Compounds containing a Propenylic Side Chain.** By J. BOUGAULT (*Ann. Chim. Phys.*, 1902, [vii], 25, 483–574).—The greater portion of the work described in this memoir has already been published (compare Abstr., 1900, i, 311, 312, 361, 495, 548, 641; 1901, i, 324, 383, 389, 392, 721).

*p-Methoxyhydratropaldehyde*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe} \cdot \text{COH}$ , obtained by the action of iodine and yellow mercuric oxide on anethole, is a colourless liquid boiling at 255–256° (corr.) and having a sp. gr. 1.069 at 15°; it is almost insoluble in water, and changes into resinous substances

on treatment with concentrated acid or alkaline solutions. The *oxime*, when crystallised from ether, melts at  $96^{\circ}$ . *p*-Methoxyhydratropic acid, produced by oxidising the preceding aldehyde with silver nitrate in alkaline solution, crystallises in monoclinic prisms; its *ammonium* salt,  $\text{NH}_4 \cdot \text{C}_{10}\text{H}_{11}\text{O}_3$ , formed by passing ammonia into an ethereal solution of the acid, crystallises in leaflets readily soluble in water. The *sodium* salt,  $\text{C}_{10}\text{H}_{11}\text{O}_3\text{Na} \cdot 2\text{H}_2\text{O}$ , crystallises in needles, the *calcium* salt,  $(\text{C}_{10}\text{H}_{11}\text{O}_3)_2\text{Ca}$ , separates from water or dilute alcohol with  $2\text{H}_2\text{O}$ , the *lead* salt,  $(\text{C}_{10}\text{H}_{11}\text{O}_3)_2\text{Pb} \cdot \text{H}_2\text{O}$ , forms white needles, the *silver* and *copper* salts are insoluble.

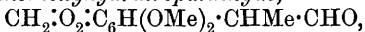
The acid contains an asymmetric carbon atom, and has been resolved into its optically active components by the aid of morphine, this alkaloid precipitating the *lævorotatory* acid in the form of a salt. The *lævorotatory* acid has  $[\alpha]_D - 67^{\circ}40'$ ; the *dextrorotatory* isomeride left in the mother liquors of the morphine salt was not obtained quite pure, the highest value for the rotatory power being  $+55^{\circ}$ .

3 : 4-Dimethoxyhydratropaldehyde,  $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CHMe} \cdot \text{CHO}$ , obtained by the action of iodine and yellow mercuric oxide on methylisoeugenol, is isolated in the form of its soluble bisulphite compound, and set free by boiling this derivative with sodium carbonate; it is soluble in the ordinary organic solvents and separates in crystals melting at  $44^{\circ}$ ; the *oxime* melts at  $77^{\circ}$ .

3 : 4-Dimethoxyhydratropic acid, prepared from the preceding aldehyde, crystallises with  $1\text{H}_2\text{O}$  and melts at  $60^{\circ}$ . The *sodium* salt,  $\text{C}_{11}\text{H}_{13}\text{O}_4\text{Na}$ , crystallises in colourless needles, the *calcium* salt is soluble in water and crystallises with  $2\text{H}_2\text{O}$ .

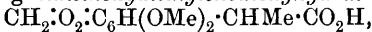
3 : 4-Dihydroxyhydratropic acid,  $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$ , results from the action of red phosphorus and hydriodic acid and melts at  $97^{\circ}$ ; in alkaline solution, it rapidly undergoes oxidation, giving a red coloration; ferric chloride develops a dark green coloration, changing to brown. 3 : 4-Dimethoxyacetophenone,  $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{COMe}$ , is prepared by oxidising the corresponding dimethoxy-aldehyde or acid with chromic acid; it melts at  $48^{\circ}$  and on treatment with alkaline potassium permanganate gives rise to 3 : 4-dimethoxyphenylglyoxylic acid.

*iso*Apiole, on oxidation with iodine and yellow mercuric oxide, yields a dimethoxymethylenedioxyhydratropaldehyde,



a colourless liquid boiling at  $305^{\circ}$  and having a sp. gr. 1.246 at  $15^{\circ}$ ; this compound is soluble in the ordinary organic solvents excepting light petroleum, and does not dissolve in water.

The corresponding dimethoxymethylenedioxyhydratropic acid,



obtained by oxidising the preceding compound with silver nitrate in alkaline solution, crystallises from water and melts at  $97^{\circ}$ ; its sodium salt,  $\text{C}_{12}\text{H}_{13}\text{O}_6\text{Na} \cdot 3\text{H}_2\text{O}$ , is soluble in alcohol. The action of chromic mixture on the preceding aldehyde results in the formation of a dimethoxymethylenedioxyacetophenone, a substance crystallising from hot water in colourless needles, melting at  $92^{\circ}$ , and yielding dimethoxymethylenedioxyphenylglyoxylic acid on oxidation with alkaline permanganate.

G. T. M.

**Isatoic Acid.** FARBWERKE VORM. MEISTER, LUCIUS, & BRUNING (D.R.-P. 127138).—Isatoic acid,  $C_6H_4 \begin{smallmatrix} \text{CO}-\text{O} \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$ , results from the action of hypochlorous acid on phthalimide in the absence of alkali hydroxides; it is precipitated by acidifying an emulsion of phthalimide and bleaching powder with dilute hydrochloric acid. The *sodium hydrogen* salt,  $CO_2H \cdot C_6H_4 \cdot NH \cdot CO_2Na$ , produced by dissolving phthalimide in dilute sodium hydroxide solution (1 mol. NaOH) and adding the equivalent amount of sodium hypochlorite solution, crystallises from this mixture in lustrous leaflets. G. T. M.

**Formation of Indoxyl from Phenylglycine-*o*-carboxylic Acid.** By DANIEL VORLÄNDER (*Ber.*, 1902, 35, 1683—1698).—[With ERICH MUMME and A. WANGERIN.]—The production of indoxyl derivatives and indigo from the esters of phenylglycine-*o*-carboxylic acid by fuming sulphuric acid and by alkaline reagents appears to depend on stereochemical relations and not on the positive or negative character of the alkyl or acyl group which is introduced. It seems probable that an intermediate product of the type  $C_6H_4 \begin{smallmatrix} \text{NR} \\ \text{C}(\text{OH})_2 \end{smallmatrix} > CH \cdot CO_2H$  is first formed.

The following derivatives of phenylglycinecarboxylic acid have been employed. *Acetylphenylglycinecarboxylic acid* melts and decomposes at 214° after previously sintering; the electrical conductivity, *K* is 0.105 at 25°. The *benzoyl* derivative melts and decomposes at 195°. *Benzosulphurylphenylglycinecarboxylic acid* crystallises in plates and melts and decomposes at 190°. *Nitrosophenylglycinecarboxylic acid* melts and decomposes at about 120°. *Dimethyl acetylphenylglycinecarboxylate* melts at 81—82° and boils with slight decomposition at 205—212° under 30 mm. pressure. The *diethyl* ester melts at 63—64° and boils at 214—218° under 15 mm. pressure. The *monoethyl* ester (aliphatic) melts at 86—87° and has the conductivity *K* 0.038 at 25°; 2.40 grams dissolve in 100 of water at 13°. The *monoethyl* ester (aromatic) melts at 130—132° and has the conductivity *K* 0.030 at 25°, the solubility being 0.41 at 13°. *Diethyl propionylphenylglycinecarboxylate* melts at 64—66°. The *diethyl* ester of the *benzoyl* derivative forms an oil which crystallises after some time and then melts at 51—52°. *Diethyl carbethoxyphenylglycinecarboxylate*, prepared from ethyl chlorocarbonate, melts at 48—50°. *Diethyl nitrosophenylglycinecarboxylate* is an oil which gradually decomposes. The *methyl* ester of the *acetonitrilic acid*, prepared from the methyl ester of anthranilic acetonitrile, melts at 81—83°. The corresponding *ethyl* ester is an oil.

The reagents which bring about condensation to indoxyl derivatives may be divided into three classes.

I. Reagents the effect of which is not much influenced by the degree of esterification or acylation. (1.) All derivatives of phenylglycinecarboxylic acid, except the nitroso-acid, its esters and benzosulphuryl-glycinecarboxylic acid, are converted into indoxyl acid and indoxyl by alkali hydroxides at temperatures above 200°. The presence of the alkali is essential, since neither the alkali salts nor the calcium or barium



salts yield any indoxyl when heated alone. (2.) Boiling with acetic anhydride and sodium acetate has no effect on the nitroso-acid and the derivatives of anthranilic acetonitrile, but is applicable to all other derivatives. This reaction may be used as a test to distinguish phenylglycine-*o*-carboxylic acid from phenylglycine and from the *m*- and *p*-carboxylic acids. The acetyl derivative gives a better yield than the free acid, whilst the dialkyl esters only give very small yields. The benzosulphuryl derivative forms a diacylindoxyl which crystallises in flat needles melting at 142°.

II. Reagents the effect of which is increased by complete esterification of the phenylglycinecarboxylic acid derivatives. (3.) Aqueous alkalis and ammonia in the cold produce traces of indoxyl derivatives from the normal esters of acyl derivatives. These can be detected by the violet or blue coloration produced by boiling with 60 per cent. sulphuric acid. (4.) Boiling dilute aqueous alkalis and baryta water produce indoxyl derivatives from the normal acyl esters, but not from the free acids or the ester acids. The best yield is obtained with 20 per cent. aqueous potash. (5.) Boiling aqueous sodium carbonate also produces indoxyl derivatives, but in much smaller yield than the alkali hydroxides. (6.) Alcoholic aqueous alkali at the ordinary temperature only produces small amounts of indoxyl derivatives, the yield varying with the amount and the concentration of the alkali and with the percentage of alcohol. Excess of alkali tends to hydrolyse the esters rather than to produce condensation. (7.) Boiling alcoholic aqueous alkali produces larger yields. (8.) Alcoholic alkali or alcoholic sodium ethoxide at the ordinary temperature produces condensation to indoxyl esters, except with anthranilic acetonitrile and its acetyl derivative. *Diethyl N-acetylindoxylate* crystallises in needles melting at 114—115°; by the continued action of excess of alkali in the cold, it passes into indoxyl ester. *Diethyl N-benzoylindoxylate* melts at 84—86°, and does not lose the acyl group so readily as the acetyl compound. These two derivatives are isomeric with those obtained by the direct acylation of the indoxyl ester, and are soluble in cold aqueous alkalis. With ferric chloride, they give a permanent green coloration, whereas the *o*-acyl derivatives give no coloration, and the indoxyl esters themselves only a temporary green coloration with this reagent. Ethyl nitrosophenylglycinecarboxylate is converted by alcoholic sodium ethoxide into indoxyl ester. The non-acylated esters yield no indoxyl derivatives with alcoholic soda, and only traces with sodium ethoxide. (9.) Boiling alcoholic sodium ethoxide acts both on acylated and non-acylated derivatives, the best results being obtained when the solid ester is added to a concentrated alcoholic solution. Indoxyl acid may be prepared with advantage by this method from diethyl phenylglycinecarboxylate. (10.) In the presence of indifferent solvents, such as benzene or ether, the condensing action of sodium ethoxide is intensified, the reaction proceeding in the cold both with acylated and non-acylated derivatives. When treated with benzene, a small amount of alcohol and metallic sodium, the phenylglycinecarboxylic ester itself, and its benzoyl derivative readily undergo condensation, whereas the acetyl derivative in these circumstances yields no indoxyl compounds.

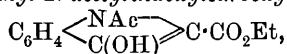
III. Reagents the effect of which is generally increased by acylation, but only slightly or not at all by esterification. (11.) When heated with anhydrous sulphuric acid or fuming sulphuric acid, the following compounds yield indigosulphonic acids: acetylphenylglycinecarboxylic acid, and its dimethyl, diethyl, and both monoethyl esters; diethyl propionylphenylglycinecarboxylate. On the other hand, the following do not yield indigo derivatives: phenylglycinecarboxylic acid and its esters, amides, and anilides; benzoylphenylglycinecarboxylic acid and its esters; the benzosulphuryl acid, the nitroso-acid and ester; the diethyl esters of the carbethoxy- and the formyl-acids, the anthranilic acetonitrile and its ester, and acetylanthranilic acetonitrile ester. This reagent may therefore be used as a test for the presence of acetyl- and propionyl-phenylglycinecarboxylic acids. The yield of indigo obtained from acetylphenylglycinecarboxylic acid is 49·7 per cent. of the theoretical, whilst that from the various esters is somewhat less. The reason for the difference between the behaviour of the acetyl and propionyl compounds on the one hand, and that of the benzoyl, formyl, carbethoxy-, and benzosulphuryl derivatives on the other, has not been ascertained.

A. H.

**Crystallised Indoxyl.** By DANIEL VORLÄNDER and B. DRESCHER (*Ber.*, 1902, 35, 1701—1702).—Indoxyl, which has hitherto been described as an uncrystallisable oil, can readily be obtained in yellow crystals by decomposing indoxyllic acid with warm water in an atmosphere of coal gas, filtering, and cooling the solution in ice-water. It melts at 85°, is very sparingly soluble in light petroleum, and partially vaporises when heated alone or with slightly superheated steam, forming a vapour which has a faecal odour. The analysis and determination of mol. weight by the cryoscopic method in benzene and acetic acid confirm the usual formula.

A. H.

**Ethereal Indoxylcarboxylates containing Acyl Groups attached to Nitrogen.** FARBERG MÜHLHEIM VORM. A. LEONHARDT (D.R.-P. 126962).—*Ethyl N-acetylindoxylcarboxylate*,



obtained by treating ethylacetylphenylglycinecarboxylate with sodium ethoxide dissolved in absolute alcohol or with alcoholic potassium hydroxide at the ordinary temperature, crystallises out from the solution and melts at 115°. The *methyl* ester melts at 117°

*Ethyl N-benzoylindoxylcarboxylate*, prepared from *ethyl benzoylphenylglycinecarboxylate* and sodium ethoxide, is obtained in yellow crystals melting at 87—88°. The glycine derivative itself is produced by heating diethyl phenylglycinecarboxylate with benzoyl chloride in toluene solution and melts at 53—54°.

The *urethanes*,  $\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{CO}_2\text{Me}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$  and  $\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{CO}_2\text{Et}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , obtained by heating diethyl phenylglycinecarboxylate with excess of methyl and ethyl chlorocarbonates respectively, melt at 60—61° and 50°, and when treated with sodium ethoxide give rise to the corresponding urethanes of the alkyl indoxylcarboxylates.

G. T. M.

**Decomposition of Coumarone by means of Alcoholic Potassium Hydroxide.** By RICHARD STOERMER and BRUNO KAHLERT (*Ber.*, 1902, **35**, 1630—1632. Compare *Abstr.*, 1901, i, 533, 535).—Among the products of the decomposition of coumarone by alcoholic potassium hydroxide (*loc. cit.*), *o*-ethylphenol has now been recognised. It is present in the lowest fraction, obtained when the mixture of phenols is distilled under reduced pressure; it boils at 92—95° under 20 mm. pressure. The higher fractions appear to contain a polymeride of *o*-hydroxystyrene. In the products insoluble in alkali hydroxide, hydrocoumarone and a hydrocarbon, possibly tetrahydronaphthalene, were recognised. K. J. P. O.

**1- and 2-Bromocoumarone.** By RICHARD STOERMER and BRUNO KAHLERT (*Ber.*, 1902, **35**, 1633—1640).—1-Bromocoumarone,  $C_6H_4 \begin{array}{c} \diagup O \\ CH \diagdown \end{array} CBr$ , is prepared by the distillation of dibromocoumarone or by the action of phosphorus oxybromide on the lactone of *o*-hydroxyphenylacetic acid; the very pale yellow oil thus obtained boils at 220—222°, has a sp. gr. 1·5403 at 18°, and a refractive index 1·5986 at 22°. 2-Bromocoumarone, (m. p. 38—39°) was obtained by the action of alcoholic potash on dibromocoumarone. When heated under pressure at 190—200° with alcoholic potash, the liquid 1-bromocoumarone is quantitatively converted into *o*-hydroxyphenylacetic acid; 2-bromocoumarone yields only a small amount of *o*-hydroxyphenylacetic acid and *o*-ethoxyphenylacetic acid; at the same time, the presence of 2-ethoxycoumarone was rendered probable among the products of the reaction.

**1-Nitrocoumarone**,  $C_6H_4 \begin{array}{c} \diagup O \\ CH \diagdown \end{array} C \cdot NO_2$ , is formed when 1-bromocoumarone is exposed to the action of nitrous fumes, and is identical with the nitro-coumarone (*Abstr.*, 1898, i, 30) obtained by the direct nitration of coumarone; it crystallises in white needles melting at 134°. By the action of nitrous fumes on 2-bromocoumarone, 2-bromonitrocoumarone (m. p. 132°) was obtained (*loc. cit.*). K. J. P. O.

**1-Nitro-coumarone and one of its Characteristic Transformations.** By RICHARD STOERMER and BRUNO KAHLERT (*Ber.*, 1902, **35**, 1640—1646. Compare preceding abstract).—On reducing an alcoholic solution of 1-nitrocoumarone with tin and hydrochloric acid, *o*-hydroxyphenylacetic acid is formed. When boiled with aqueous alkali hydroxides, 1-nitrocoumarone is converted into salicylic acid, hydrogen cyanide, and nitrous acid. If sodium ethoxide is employed, an intermediate product, *benzoximinoketolactone*,  $C_6H_4 \begin{array}{c} \diagup O \\ CO \diagdown \end{array} C \cdot NOH$ , is obtained, which crystallises in white needles melting and decomposing at 172°, and is soluble in aqueous alkalis with an intense yellow colour. With phenylhydrazine, a *phenylhydrazoxime*,  $C_{14}H_{11}O_2N_3$ , is obtained as lemon-yellow crystals melting at 155—156°.

When an alkaline solution of the oximinoketolactone is boiled, salicylic acid is formed. By boiling hydrochloric acid, the oximinoketolactone is converted into hydroxylamine and *o*-hydroxybenzoyl-

formic acid, to which the formula  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}_2\text{H}$  is assigned; it is found to melt at  $39\cdot5^\circ$ ; *o*-hydroxyphenylisonitrosoacetic acid, obtained from the benzoylformic acid, melted and decomposed at  $149^\circ$  (compare Baeyer and Fritsch, Abstr., 1884, 1021). K. J. P. O.

[6:6'-Dichloroindigotin.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 128727).—The presence of halogen radicles in the meta-positions with respect to the carbonyl groups of the indigo molecule does not affect the general properties and the colour of this pigment. If, however, chlorine atoms are introduced into the para-positions with respect to carbonyl, then a reddish-violet colouring matter is produced.

6:6'-Dichloroindigotin, prepared from *p*-chloro-*o*-nitrobenzaldehyde (m. p.  $67\text{--}68^\circ$ ) by condensation with acetone in sodium hydroxide solution, is a brownish-red powder with a metallic lustre; it is insoluble in the ordinary solvents, but dissolves in boiling nitrobenzene or aniline to a deep red solution. Its vapour is deep red and on cooling yields the substance in a crystalline form. 6:6'-Dichloroindigotin, when treated with fuming sulphuric acid, forms a soluble sulphonic acid the barium salt of which is sparingly soluble. The dichloroindigotin may be treated in the ordinary indigo "vat," and gives reddish-violet shades on cotton and wool.

The intermediate ketone,  $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{COMe}$ , has also been isolated. G. T. M.

Diacetylindigo-white. DANIEL VORLÄNDER & BRUNO DRESCHER (D.R.-P. 126799. Compare Liebermann and Dickhuth, Abstr., 1892, 480).—Diacetylindigo-white is readily obtained in quantitative yield by shaking up an aqueous or acetone solution of a salt of indigo-white with acetic anhydride; it crystallises from water or acetone in white needles, becoming violet at  $205^\circ$  and decomposing at  $215\text{--}230^\circ$ . A tetra-acetyl derivative, which melts at  $258^\circ$ , is produced by warming the compound with acetic anhydride and sodium acetate. G. T. M.

Diphenyltetrenecarboxylic Acid. By THEODOR LANSEK and B. F. HALVORSEN (*Ber.*, 1902, 35, 1407—1411).—This acid is shown to have the constitution  $\begin{array}{c} \text{CPh}\cdot\text{C}\cdot\text{CO}_2\text{H} \\ | \\ \text{CPh}\cdot\text{C}\cdot\text{CO}_2\text{H} \end{array}$ , as assumed by Manthey (Abstr., 1901, i, 31), and is not a triphenyltrimesic acid, as previously supposed (Abstr., 1899, i, 916). The "partial anhydride,"  $\text{C}_{27}\text{H}_{16}\text{O}_5$ , formerly described, is in reality the complete anhydride,  $\text{C}_{18}\text{H}_{10}\text{O}_3$ .

Monomethyl diphenyltetrenedicarboxylate,  $\begin{array}{c} \text{CPh}\cdot\text{C}\cdot\text{CO}_2\text{H} \\ | \\ \text{CPh}\cdot\text{C}\cdot\text{CO}_2\text{Me} \end{array}$ , obtained by hydrolysing the dimethyl ester with sodium dissolved in methyl alcohol, crystallises from alcohol in small, white needles and melts and decomposes at  $207^\circ$ ; the silver salt,  $\text{C}_{19}\text{H}_{18}\text{O}_4\text{Ag}$ , is a white powder. The analogous ethyl ester,  $\text{C}_{20}\text{H}_{16}\text{O}_4$ , crystallises similarly and melts and decomposes at  $207^\circ$ . Both esters, when heated above the melting point, lose alcohol and yield the anhydride of the acid.

Attempts to prepare the amide of the acid failed, but on passing gaseous ammonia into a benzene solution of the anhydride, the

ammonium salt,  $\begin{matrix} \text{CPh}:\text{C}:\text{CO}\cdot\text{NH}_2 \\ | \\ \text{CPh}:\text{C}:\text{CO}_2\cdot\text{NH}_4 \end{matrix}$ , of the acid amide is obtained as a white, voluminous precipitate; the analogous silver salt,  $\text{C}_{18}\text{H}_{12}\text{O}_3\text{NaAg}$ , was analysed. Diphenyltetrenedicarboxylimide,  $\begin{matrix} \text{CPh}:\text{C}:\text{CO} \\ | \\ \text{CPh}:\text{C}:\text{CO} \end{matrix} > \text{NH}$ , obtained by subliming the anhydride in dry ammonia, crystallises from alcohol in feathery aggregates of needles and melts at  $246^\circ$ .

The fluorescein,  $\begin{matrix} \text{CPh}:\text{C} \\ | \\ \text{CPh}:\text{C}:\text{CO}\cdot\text{O} \end{matrix} - \text{C}:[\text{C}_6\text{H}_3(\text{OH})_2]\cdot\text{O}$ , obtained from diphenyltetrenedicarboxylic acid by fusing its anhydride with resorcinol, crystallises from toluene. W. A. D.

**Some Amyl Esters of Substituted Phthalic Acids.** By WILHELM MARCKWALD (*Ber.*, 1902, 35, 1602—1606).—1-*iso*-Amyl hydrogen 3-nitrophthalate melts at  $93\cdot5^\circ$ , and again melts at the same point if solidified only a few degrees below this temperature; if, however, the liquid be cooled rapidly to  $70^\circ$ , it solidifies, and the product melts and remelts at  $78^\circ$ , the melting point only rising to  $93\cdot5^\circ$  after the solid mass has been left for several hours. The ester is thus dimorphous, and melting point curves are given which show that the labile form melting at  $78^\circ$  is isomorphous with the isomeric 1-*d*-amyl hydrogen 3-nitrophthalate; as, however, the labile form is not produced in quantity when the inactive ester is prepared from *iso*-amyl alcohol containing 20 per cent. of the active alcohol, a single crystallisation of the product effects a complete separation.

2-*iso*-Amyl hydrogen 3-nitrophthalate melts at  $161$ — $162^\circ$ ,  $4^\circ$  lower than stated by McKenzie (*Trans.*, 1901, 79, 1135); 2-*d*-amyl hydrogen 3-nitrophthalate, obtained by heating 3-nitrophthalic anhydride with pure *d*-amyl alcohol, crystallises from benzene in silvery leaflets, melts at  $154$ — $155^\circ$ , and has  $[\alpha]_D + 2\cdot6$  in acetone solution. A curve is given showing the melting points of mixed crystals of the *iso*-amyl and *d*-amyl esters.

*iso*-Amyl hydrogen tetrachlorophthalate crystallises from carbon disulphide in stout, vitreous prisms, and melts at  $112$ — $113^\circ$ ; the analogous *d*-amyl ester separates from light petroleum in opaque crystals and melts at  $94$ — $95^\circ$ . In spite of their solubility in light petroleum being very different, the salts are only separated with great difficulty by crystallisation from this solvent owing to the formation of mixed crystals; a curve is given showing the variation in the melting point of such crystals. W. A. D.

**Unsaturated Dicarboxylic Acids from Ketones and Diethyl Succinate.** By HANS STOBBE (*Annalen*, 1902, 321, 83—93. Compare *Abstr.*, 1899, i, 900, 901, 902; 1900, i, 179; 1901, i, 149, 276, 549, and succeeding abstracts).—A theoretical discussion of the experimental results indicated in the two following abstracts, from which the following rules are deduced.

1. In condensing ketones with diethyl succinate,  $\gamma\delta$ -unsaturated acids (alkylidenepyrotartaric acids) are the principal products when the

ketones contain the methylene radicle, whereas ketones in which this group is absent give rise to  $\beta\gamma$ -acids (substituted itaconic acids).

2. The tendency to form alkylidene pyrotartaric acids is greater in the ketones containing a methylene residue combined with an aromatic nucleus than in those in which methylene is attached to aliphatic radicles.

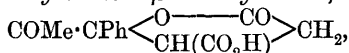
G. T. M.

### Condensation of Propiophenone with Diethyl Succinate.

By HANS STOBBE and KARL NIEDENZU (*Annalen*, 1902, 321, 94—100. Compare preceding abstract).— $\gamma$ -Phenyl- $\gamma$ -ethylidenepyrotartaric acid,  $\text{CHMe} \cdot \text{CPh} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , produced by condensing propiophenone with ethyl succinate in the presence of sodium ethoxide suspended in dry ether, is isolated in the form of its *barium* salt,  $\text{C}_{13}\text{H}_{12}\text{O}_4\text{Ba}$ , a substance which crystallises in silky, colourless needles. The free acid crystallises from hot water in colourless, monoclinic needles readily soluble in the ordinary organic solvents excepting light petroleum and carbon disulphide; it melts at  $137$ — $138^\circ$ . The *calcium* salt,  $\text{C}_{13}\text{H}_{12}\text{O}_4\text{Ca} \cdot \text{H}_2\text{O}$ , is a crystalline powder, the *silver* salt,  $\text{C}_{13}\text{H}_{12}\text{O}_4\text{Ag}_2$ , a curdy precipitate.

When oxidised with 3 atoms of oxygen derived from potassium permanganate, the preceding acid gives rise to  $\beta$ -benzoylpropionic and acetic acids together with a trace of benzoic acid.

$\gamma$ -Acetyl- $\gamma$ -phenylbutyrolactone- $\beta$ -carboxylic acid,



is also produced in the preceding oxidation, but is obtained in better yield when only 2 atoms of oxygen are employed; it crystallises from water containing a few drops of sulphuric acid in well-defined monoclinic prisms melting at  $141$ — $142^\circ$ . The existence of a lactone ring in this acid is demonstrated by titrations with *N*/10 hydrochloric acid and potassium hydroxide. The *barium* salt,  $(\text{C}_{13}\text{H}_{11}\text{O}_5)_2\text{Ba}$ , of the lactone-acid is soluble in absolute alcohol, whilst the *barium* salt,  $\text{C}_{13}\text{H}_{12}\text{O}_6\text{Ba}$ , of the hydroxy-dicarboxylic acid is insoluble in this medium; the latter substance results from the fission of the lactone ring and they are both obtained on treating the lactone-acid with freshly precipitated barium carbonate.

The *semicarbazons*,  $\text{C}_{14}\text{H}_{15}\text{O}_5\text{N}_3$ , of the lactone-acid produced by the action of semicarbazide hydrochloride and sodium acetate separates from dilute alcohol in granular crystals decomposing at  $210^\circ$ . Prolonged treatment of the lactone-acid with permanganate solution leads to the production of benzoylpropionic and acetic acids.

Two stereoisomeric substances,  $\gamma$ -phenyl- $\gamma$ -ethylitaconic acid and  $\gamma$ -phenyl- $\gamma$ -ethylisoitaconic acid, are obtained in the condensation of propiophenone and ethyl succinate, and are isolated in the mother liquors after the separation of the substituted pyrotartaric acid.

$\gamma$ -Phenyl- $\gamma$ -ethylitaconic acid,  $\text{CEtPh} \cdot \text{C}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , crystallises from hot water in triclinic prisms and decomposes at  $175$ — $176^\circ$ ; it is sparingly soluble in water or benzene, and is separated from its isomeride by fractional crystallisation from these solvents. The *calcium* salt,  $\text{C}_{13}\text{H}_{12}\text{O}_4\text{Ca}$ , is a granular precipitate.

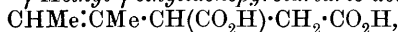
$\gamma$ -Phenyl- $\gamma$ -ethylisocitaconic acid separates from its aqueous solution in comb-like aggregates of triclinic plates decomposing at  $184-184.5^\circ$ ; the crystals differ entirely from those of the stereoisomeride in shape, and in angle of extinction. The calcium salt is described.

The two stereoisomeric acids, when oxidised with potassium permanganate in sodium carbonate solution, yield the same products, namely, propiophenone with traces of acetic and oxalic acids.

G. T. M.

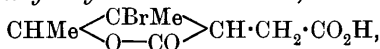
### Condensation of Methyl Ethyl Ketone with Ethyl Succinate

By HANS STOBBE, ARTHUR STRIGEL, and CARL MEYER (*Annalen*, 1902, 321, 105—126).— $\gamma$ -Methyl- $\gamma$ -ethylidenepyrotartaric acid,



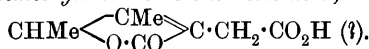
formerly called methylethylsuccinic acid (compare *Abstr.*, 1895, i, 143), is the chief product of the condensation between methyl ethyl ketone and ethyl succinate; its electrical conductivity,  $\mu_\infty$ , is 351, and its dissociation constant,  $K$ , is 0.0112. The normal potassium salt,  $\text{C}_8\text{H}_{10}\text{O}_4\text{K}_2$ , crystallises in lustrous spangles, the potassium hydrogen salt,  $\text{C}_8\text{H}_{11}\text{O}_4\text{K}\cdot\text{H}_2\text{O}$ , separates from dilute alcohol in well-defined, rhombic plates. When treated with an alkaline solution of potassium permanganate, the acid yields a mixture of lævulic and acetic acids, about 20 per cent. of the original substance remaining unchanged.

$\beta$ -Bromo- $\beta$ - $\gamma$ -dimethylbutyrolactoneacetic acid,

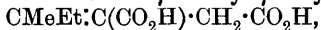


formerly known as  $\gamma$ -methyl- $\gamma$ -ethyl- $\beta$ -bromoparaconic acid, results from the action of bromine on the preceding acid dissolved in chloroform; it melts at  $161^\circ$ , and when left in contact with cold sodium hydroxide solution, or when boiled with this reagent, gives rise to the dilactone,

$\begin{array}{c} \text{CHMe}\cdot\text{CMe} \\ \diagdown \text{O} \diagup \text{CO} \end{array} \cdot \text{CH}\cdot\text{CH}_2\cdot\text{CO} \cdot \begin{array}{c} \text{O} \\ \diagup \text{CO} \diagdown \end{array} \text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  $\gamma\delta$ -dihydroxy- $\gamma$ -methyl- $\gamma$ -ethylpyrotartaric acid, and  $\beta$ - $\gamma$ -dimethylcrotonolactoneacetic acid,

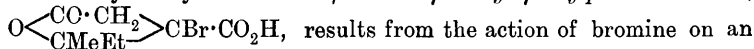


The former of these substances is insoluble in sodium carbonate solution but dissolves readily in hot water or chloroform, and more sparingly in carbon disulphide or ether; it separates in rhombic crystals and melts at  $147-148^\circ$ . When treated with potassium hydroxide, the dilactone reacts as a hydroxymonolactonecarboxylic acid, only one of the lactone rings undergoing fission. Excess of barium hydroxide solution (3 mols.) leads to the disruption of both lactone rings, the barium salt obtained having the composition  $\text{C}_6\text{H}_{10}(\text{OH})_2(\text{CO}_2)_2\text{Ba}$ .  $\beta\gamma$ -Dimethylcrotonolactoneacetic acid, the chief product of the hydrolysis of the bromo-acid, separates from ether in short prisms or plates and melts at  $144-145^\circ$ .  $\gamma$ -Methyl- $\gamma$ -ethylitaconic acid,

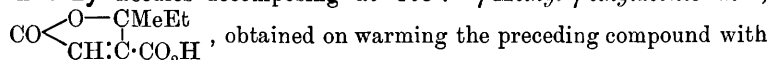


the bye-product of the condensation between methyl ethyl ketone and ethyl succinate, is less soluble than  $\gamma$ -methyl- $\gamma$ -ethylidenepyrotartaric acid, and is purified by crystallisation from acetone; it melts and decomposes at  $181^\circ$ . Its electrical conductivity,  $\mu_\infty$ , is 351, the calculated dissociation constant,  $K$ , being 0.0150. The substance may be

titrated as a dibasic acid; the *barium* salt,  $C_8H_{10}O_4Ba$ , crystallises in small plates and the silver salt is a flocculent, white precipitate soluble in hot water and sensitive to light. On oxidation with alkaline permanganate solution, the acid yields a mixture of oxalic and acetic acids with methyl ethyl ketone. *β-Bromo-γ-methyl-γ-ethylparaconic acid*,

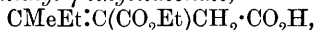


aqueous suspension of the preceding acid; it crystallises from benzene in silky needles decomposing at  $163^\circ$ . *γ-Methyl-γ-ethylaconic acid*,



sodium hydroxide solution, crystallises from water in lustrous scales melting at  $117\text{--}119^\circ$ ; it is readily soluble in the ordinary organic solvents, and its alkaline solution decolorises permanganate. The lactone ring in this substance is very stable; the acid is exactly neutralised by one equivalent of potassium hydroxide, and the *barium* salt,  $(C_8H_9O_4)_2Ba$ , obtained by the action of excess of barium hydroxide, shows that the compound is a monobasic acid. Fission of the lactone ring occurs only on boiling the acid with excess of alkali hydroxide solution. A rapid titration of the solution with standard acid indicates that the neutralisation of the free alkali induces the regeneration of the lactone so that the neutralised solution is again rendered alkaline, the alkalinity increasing rapidly when the solution is allowed to remain for some time before the final titration. An exactly neutralised solution is found to contain after 24 hours 95.70 per cent. of the lactone-acid, and only 4.30 per cent. of the hydroxy-dicarboxylic acid. The volumetric results and the properties of the two unsaturated dicarboxylic acids and their derivatives are summarised in tabular form.

*Ethyl hydrogen γ-methyl-γ-ethylitaconate*,



is obtained as an oil on distilling in steam the products of the condensation; it is accompanied by a certain quantity of the free acid, the two substances being separated by the difference in solubility of their potassium salts in absolute alcohol. The salt of the acid-ester dissolves in this solvent, whilst the potassium methylethylitaconate is insoluble. The acid ester boils at  $171\text{--}177^\circ$  under 15 mm. pressure and is very unstable, being converted into the corresponding acid. The *barium* salt,  $(\text{CO}_2\text{Et} \cdot C_6H_{10} \cdot \text{CO}_2)_2Ba$ , is amorphous and soluble in water or alcohol.

G. T. M.

**Separation of Phenylparaconic Acid into its Optically Active Components.** By AD. KREUTZ (*Annalen*, 1902, 321, 127—139).—*l-Phenylparaconic acid*,  $C_{11}H_{10}O_4$ , obtained from the strychnine salt, which is precipitated by the addition of the finely powdered alkaloid to a solution of *r*-phenylparaconic acid (m. p.  $99^\circ$ ) in absolute alcohol, crystallises from water in flexible needles and from the organic solvents in lustrous leaflets; it separates with  $\frac{1}{4}$  mol.  $H_2O$ , like the racemic compound, and melts indefinitely at  $125\text{--}131^\circ$ . The acid has  $[\alpha]_D - 59.3^\circ$  in dilute alcohol; the *strychnine* salt is sparingly soluble in cold water or alcohol, but dissolves more readily in hot water; it



softens at  $198^{\circ}$  and melts at  $202-203^{\circ}$ . The calcium salt,  $(C_{11}H_9O_4)_2Ca$ , crystallises in needles; the *barium* salt separates in needles containing  $3H_2O$ ; the *silver* salt is stable to light and forms druses of small needles. *Sodium* 1-phenylparaconate has  $[\alpha]_D -53.11^{\circ}$ , whilst the *sodium* salt of the corresponding hydroxy-acid (1-phenylitamic acid) has  $[\alpha]_D -17.19^{\circ}$ ; the free hydroxy-acid set free in ice-cold solutions has  $[\alpha]_D -12.29^{\circ}$ . The hydroxy-acid and its salt are therefore much less active than the corresponding lactone derivatives.

d-Phenylparaconic acid is obtained in the form of its strychnine salt from the final mother liquor obtained in crystallising strychnine 1-phenylparaconate; the free acid,  $C_{11}H_{10}O_4, \frac{1}{2}H_2O$ , resembles its optical antipode and melts between  $115^{\circ}$  and  $131^{\circ}$ ; it has  $[\alpha]_D +56.9^{\circ}$  in 50 per cent. alcohol. The strychnine salt separates in ill-defined crystals melting at  $100-102^{\circ}$ ; the *barium*, *calcium*, and *silver* salts closely resemble those of the lævorotatory acid.

*Sodium* d-phenylparaconate and *sodium* d-phenylitamate have  $[\alpha]_D +57.35^{\circ}$  and  $+25.15^{\circ}$  respectively. *Barium* d-phenylitamate,  $C_{11}H_{10}O_5Ba$ , crystallises from hot water with  $1H_2O$ ; the optically active phenylparaconic acids behave like the racemic compound on distillation and give rise to phenylisocrotonic acid and  $\alpha$ -naphthol. G. T. M.

**Esters of Phloroglucinolcarboxylic Acids.** By JOSEF HERZIG and FRANZ WENZEL [and, in part, RUDOLF TÖLK and BRUNO GRAETZ] (*Monatsh.*, 1902, 23, 81—118. Compare Abstr., 1901, i, 473).—The action of diazomethane on phloroglucinolcarboxylic acid in ethereal solution leads to the formation of methyl phloroglucinolcarboxylate and methyl methoxy-, dimethoxy-, and trimethoxy-phloroglucinolcarboxylates. Methyl phloroglucinolcarboxylate is now found to melt at  $174-176^{\circ}$ . The methyl methoxyphloroglucinolcarboxylate is identical with that previously described. Methyl dimethoxyphloroglucinolcarboxylate,  $OH \cdot C_6H_2(OMe)_2 \cdot CO_2Me$ , crystallises from methyl alcohol in colourless needles and melts at  $107-109^{\circ}$ . Methyl trimethoxyphloroglucinolcarboxylate,  $C_6H_2(OMe)_3 \cdot CO_2Me$ , is best prepared by the action of methyl iodide and potassium hydroxide on methyl dimethoxyphloroglucinolcarboxylate; it crystallises in white needles and melts at  $67-70^{\circ}$ . It is also formed along with a small quantity of dimethoxyphloroglucinol and a substance melting at  $185-187^{\circ}$ , which may be methyl dimethoxyphloroglucinoldicarboxylate, by the action of methyl chlorocarbonate on trimethoxyphloroglucinol in presence of aluminium chloride.

Dimethoxyphloroglucinolcarboxylic acid,  $OH \cdot C_6H_2(OMe)_2 \cdot CO_2H$ , is prepared by the hydrolysis of its methyl ester by concentrated sulphuric acid at  $80^{\circ}$ , or by dilute alcoholic potassium hydroxide; it forms colourless needles which decompose at  $152-154^{\circ}$ . It is also formed by heating the sodium derivative of dimethoxyphloroglucinol with carbon dioxide under pressure.

Methyl trimethoxyphloroglucinolcarboxylate evolves carbon dioxide when treated with concentrated sulphuric acid. It may be hydrolysed by the action of metallic sodium in xylene solution. Trimethoxyphloroglucinolcarboxylic acid crystallises from alcohol in colourless needles which melt with decomposition at  $140-141^{\circ}$ . The action of diazo-

methane on methylphloroglucinolcarboxylic acid leads to the formation of methyl methylphloroglucinolcarboxylate and methyl methoxymethylphloroglucinolcarboxylate.

*Methyl methylphloroglucinolcarboxylate*,  $C_6HMe(OH)_3 \cdot CO_2Me$ , melts at  $144-145^\circ$ ; with sodium acetate and acetic anhydride, it yields a *triacetyl* derivative which melts at  $103-104^\circ$ . Hydrolysis of the triacetyl derivative by concentrated sulphuric acid results apparently in polymerisation (compare Abstr., 1899, i, 31). *Methyl methoxymethylphloroglucinolcarboxylate*,  $OMe \cdot C_6HMe(OH)_2 \cdot CO_2Me$ , melts at  $132-133^\circ$ ; it yields a *diacetyl* derivative which melts at  $75-77^\circ$ .

When dimethylphloroglucinolcarboxylic acid is treated with diazomethane, it yields methyl dimethylphloroglucinolcarboxylate and *methyl methoxydimethylphloroglucinolcarboxylate*,  $OMe \cdot C_6Me_2(OH)_2 \cdot CO_2Me$ , which melts at  $96-98^\circ$ , and on hydrolysis by dilute alcoholic potassium hydroxide yields *methoxydimethylphloroglucinolcarboxylic acid*, melting with evolution of carbon dioxide at  $156-157^\circ$ .

*Methoxydimethylphloroglucinol*, formed by boiling the carboxylic acid with water, or by hydrolysis of the methyl ester by an excess of potassium hydroxide, melts at  $147-148^\circ$ . Being isomeric with Bosse's dimethylphloroglucinol methyl ether (Abstr., 1901, i, 207), it must have the constitution  $[Me_2 : OMe : (OH)_2 = 1 : 3 : 2 : 4 : 6]$ .

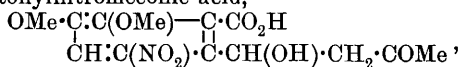
Methyl dimethylphloroglucinolcarboxylate is formed by the action of methyl iodide on silver methylphloroglucinolcarboxylate or on silver dimethylphloroglucinolcarboxylate; in the latter case, no methylation of the benzene nucleus takes place.

Methoxyphloroglucinolcarboxylic acid and methyl iodide, in presence of a slight excess of sodium methoxide, yield *methoxymethylphloroglucinolcarboxylic acid*, which melts, with evolution of carbon dioxide, at  $147^\circ$ . When boiled with water, the acid loses carbon dioxide, and yields a methoxymethylphloroglucinol, which is identical with that described by Boehm (Abstr., 1899, i, 32), and has the constitution  $[OMe : Me : (OH)_2 = 1 : 2 : 3 : 5]$ .

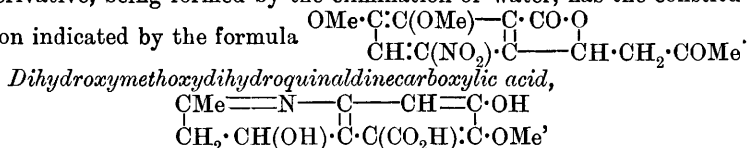
By further treatment of methoxymethylphloroglucinolcarboxylic acid with methyl iodide and sodium methoxide, there are obtained its methyl ester, a substance melting at  $205-207^\circ$ , which is probably Boehm's methyl ether of filicic acid (Abstr., 1899, i, 804), and a thin syrup which, on standing, deposits crystals of methoxytetramethylphloroglucinol, and on hydrolysis with excess of potassium hydroxide yields tetramethylphloroglucinol.

G. Y.

**Action of Acetone on Nitro-opianic Acid.** By G. Book (Ber., 1902, 35, 1498-1502. Compare Liebermann, Abstr., 1886, 468).—*Acetonynitromeconin*, produced together with tetramethoxyindigotindicarboxylic acid (opianindigo) by the action of acetone on nitro-opianic acid, is separated from the sodium salt of the indigo derivative by dissolving the latter in cold water; it crystallises in pale yellow needles and melts at  $175^\circ$ . The initial product of the condensation is probably acetonynitromeconic acid,

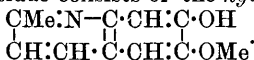


this substance which has not yet been isolated being the parent compound both of opianindigo and acetonylnitromeconine. The latter derivative, being formed by the elimination of water, has the constitution indicated by the formula



produced by reducing the preceding compound with tin and hydrochloric acid, is obtained as a white, granular precipitate melting at  $212^\circ$ ; it has both basic and acidic properties, dissolving in alkaline and ammoniacal solutions and yielding an aurichloride and a crystalline platinichloride. The formation of this substance is attended by the reduction of the nitro-group and the elimination of one methyl radicle in the form of methyl chloride.

When a solution of the preceding acid is repeatedly evaporated to dryness with hydrochloric acid, the final residue consists of the *hydrochloride* of a new *hydroxymethoxyquinaldine*,



The *platinichloride* of this base crystallises from water in long, yellow needles. G. T. M.

**Compounds from Lichens. IX.** By WILHELM ZOPF (*Annalen*, 1902, 321, 37—61. Compare Abstr., 1901, i, 87, 547).—*Lecidea confluens*, unlike so many other lichens, seems to contain only one acidic substance, namely, confluentin (m. p.  $147-148^\circ$ ). The name *picrolichenic acid* is suggested for picrolichenin; this substance melts at  $178^\circ$ , dissolves in solutions of the alkali carbonates, being reprecipitated by acids; it readily gives rise to resinous products, even in alcoholic solution, at the ordinary temperature. *Pertusaria lactea*, found at high altitudes in Tessin and the Tyrol, yields lecanoric acid and a new compound, *variolaric acid*, which is obtained only in very small amount; it melts at  $285^\circ$ , and develops violet and orange-red colorations with ferric chloride and calcium hypochlorite respectively. Rhizocarpic and pleopsidic acids are obtained from *Acarospora chlorophana*, the latter substance crystallising in tetragonal pyramids. *Hæmatomma coccineum* (var. *leiphæmum*), a greyish-white or green lichen, seems to be a distinct variety of the yellow *H. coccineum*, for it does not yield any usnic acid, and furnishes a new compound, *leiphæmum*, which melts at  $193^\circ$ , and is insoluble in alkali hydroxide solutions. Both varieties contain atranoric acid and zeorin.

*Parmelia glomellifera* contains a new substance, *glomelliferin*, which crystallises in rosettes of white needles and slowly decomposes in benzene solution, giving rise to *glomellic acid* and a compound having the properties of sphærophorin. The new acid melts at  $123-124^\circ$ , and crystallises from chloroform in short plates or prisms and from benzene in druses of fusiform crystals; it dissolves in solutions of the alkali hydroxides and carbonates and develops a violet coloration with ferric chloride. Glomelliferin is also decomposed by cold potassium hydroxide solution into glomellic acid and a substance giving a red

coloration with calcium hypochlorite and melting at  $141^{\circ}$ ; another compound, *glomellin*, is also isolated among the products of this hydrolysis; it crystallises in rhombic plates and melts at  $92^{\circ}$ .

Olivetoric acid, obtained from *Parmelia olivetorum*, melts at  $141$ – $142^{\circ}$ , and gives rise to a characteristic colour reaction with barium peroxide solution, first becoming lemon-yellow and then green without dissolving in the reagent. Lecanoric acid, which has been confounded with this compound, melts at  $166^{\circ}$  and dissolves in barium peroxide solution without developing any coloration. Moreover, when heated with methyl alcohol at  $150^{\circ}$ , lecanoric acid yields methyl orsellate (m. p.  $128^{\circ}$ ), whilst olivetoric acid gives rise to a substance melting below  $100^{\circ}$  which still gives the barium peroxide reaction (compare Hesse, Abstr., 1901, i, 149).

*Parmelia perlata*, which gives rise to atranoric and hæmatommic acids, also furnishes a third acid which is identical with the imbricatic acid formerly obtained from *P. lacarnensis*. When pure, this acid crystallises in obliquely truncated prisms and melts at  $115^{\circ}$ .

G. T. M.

[Derivatives of] *p*-Chlorobenzaldehyde. By REINHOLD VON WALTHER and W. RAETZE (*J. pr. Chem.*, 1902, [ii], 65, 258–290).—*p*-Chlorobenzaldehyde was obtained from *p*-aminobenzaldehyde by Sandmeyer's reaction and its reactions compared with those of benzaldehyde. Neither the formation of a chlorobenzoin nor a chlorohydrobenzamide was observed, although the action of ammonia on the chlorobenzaldehyde produced a very unstable compound melting at  $86$ – $90^{\circ}$ . The following condensation compounds with amines are described.

*p*-Chlorobenzylideneaniline forms yellow, slender leaflets melting at  $62^{\circ}$ . *p*-Chlorobenzylidene-*p*-toluidine crystallises in lustrous white leaflets melting at  $125^{\circ}$ . *p*-Chlorobenzylidene-*m*-toluidine forms leaflets melting at  $32^{\circ}$ . *p*-Chlorobenzylidene-*o*-toluidine forms needles melting at  $35.5^{\circ}$ . *p*-Chlorobenzylidene-*p*-chloroaniline crystallises in yellow needles or lustrous leaflets and melts at  $112^{\circ}$ . *p*-Chlorobenzylidene-*m*-chloroaniline forms felted needles melting at  $67^{\circ}$ . *Di-p*-chlorobenzylidenbenzidine forms yellowish laminæ melting at  $264^{\circ}$ . *Di-p*-chlorobenzylidene-*p*-phenylenediamine crystallises in leaflets and melts at  $200^{\circ}$ .

*p*-Chloromandelonitrile is a yellow oil. *p*-Chlorophenyl- $\alpha$ -chloroacetic acid crystallises in white leaflets and melts at  $118^{\circ}$ . The nitrile condenses with amines, forming the following compounds, which can be also obtained by the addition of hydrogen cyanide to the Schiff's bases previously described. *m*-Chloroanilino- $\alpha$ -*p*-chlorophenylacetoneitrile,  $C_6H_4Cl \cdot NH \cdot CH(C_6H_4Cl) \cdot CN$ , forms small leaflets melting at  $88^{\circ}$ . *Anilino- $\alpha$ -p*-chlorophenylacetoneitrile, crystallises in slender, white needles and melts at  $112^{\circ}$ ; the corresponding amide forms microscopic needles melting at  $145^{\circ}$ , and the acid crystallises in small, slender needles melting and decomposing at  $202^{\circ}$ .  *$\alpha$ -p*-Toluidino-*p*-chlorophenylacetoneitrile forms small, white leaflets melting at  $80^{\circ}$ ; the corresponding amide crystallises in slender, white needles melting at  $132^{\circ}$ , and the acid in leaflets melting and decomposing at  $186^{\circ}$ .  *$\alpha$ -m*-Toluidino-*p*-chlorophenylacetoneitrile forms white, lustrous leaflets melting at  $105^{\circ}$ ; the corre-

sponding *amide* is a crystalline powder which melts at 137—138°; the *acid* is a crystalline powder melting and decomposing at 180°. *α-o-Toluidino-p-chlorophenylacetoneitrile* forms colourless needles melting at 106°; the corresponding *amide* forms white, felted needles melting at 127°. *o-Carboxyanilino-α-phenylacetoneitrile* crystallises in yellow needles, melts and decomposes at 166°; the corresponding *amide* is a yellowish powder melting at 236°, and the *acid* a white, crystalline powder melting and decomposing at 184—186°. *Benzidinedi-p-chloromandelonitrile* is a yellow, crystalline powder melting at 237°. *p-Phenylene-diaminodi-p-chlorobenzyl cyanide* melts at 190°.

The aldehyde condenses with acetone, forming *p-chlorobenzylideneacetone*, which crystallises in white needles, melts at 50—51°, and yields a *phenylhydrazone* melting at 160°, and an *oxime* crystallising in slender, white needles. *p-Chlorobenzylideneacetophenone* crystallises in yellow needles, melts at 103—104°, and yields an *oxime* melting at 153°.

*p-Chlorobenzaldehyde* condenses with benzyl cyanide in the presence of sodium ethoxide, forming *α-phenyl-p-chlorocinnamonitrile*, which crystallises in silky leaflets melting at 108°, and when treated with sodium in alcoholic solution yields dibenzyl. *α-p-Nitrophenyl-p-chlorocinnamonitrile* crystallises in slender, yellow needles melting at 180°. When heated with phenylacetic acid, *p-chlorobenzaldehyde* yields *p-chlorostilbene*, which crystallises in lustrous white leaflets melting at 127°; when treated with ethyl cyanoacetate and sodium ethoxide, it yields *ethyl α-cyano-p-chlorocinnamate*, which melts at 93°, and when hydrolysed yields the *acid* melting at 196°; the corresponding *methyl ester* crystallises in slender, felted needles and melts at 121°.

*Ethyl 4-p-chlorophenyldihydrolutidinedicarboxylate*, obtained by the condensation of *p-chlorobenzaldehyde* (1 mol.) with ethyl acetoacetate (2 mols.) and ammonia, crystallises in compact tablets melting at 147°, and when oxidised by nitrous acid yields *ethyl 4-p-chlorophenyl-lutidine-dicarboxylate*, which crystallises in long, white needles melting at 67°, and when hydrolysed gives the *acid*, which is an insoluble powder, melting at 274°.

R. H. P.

**Atmospheric Oxidation of *m*-Hydroxybenzaldehydephenylhydrazone and its Derivatives.** By HEINRICH BILTZ and OTTO KAMMANN (*Annalen*, 1901, 321, 32—37. Compare next page).—When oxidised by a current of air in alcoholic potassium hydroxide solution, *m*-hydroxybenzaldehydephenylhydrazone gives rise to tarry products.

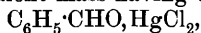
*2:4:6-Trichloro-3-hydroxybenzaldehydephenylhydrazone* crystallises from dilute alcohol in yellowish-brown needles, melts at 59—60° and does not yield an osazone by atmospheric oxidation in an alcoholic solution of potassium hydroxide.

*2:4:6-Tribromo-3-hydroxybenzaldehydephenylhydrazone*, obtained in yellowish-brown crystals melting at 129°, yields a *diacetyl* derivative separating from glacial acetic acid in yellow crystals and melting at 107—110°. Oxidation experiments made on the preceding phenylhydrazone and on the corresponding derivative of tetrachloro-*m*-hydroxybenzaldehyde do not lead to the formation of osazones.

G. T. M.

**Formation of Acetals from Hydroxynitriles.** By ROBERT STOLLÉ (*Ber.*, 1902, 35, 1590—1591).—On attempting to free freshly prepared mandelonitrile from water by filtration, it was converted into the compound  $\text{CHPh}(\text{O} \cdot \text{CHPh} \cdot \text{CN})_2$ , which crystallises from alcohol, melts at  $196.5^\circ$ , and is easily obtained by mixing benzaldehyde and mandelonitrile with alcohol containing 1 per cent. of hydrogen chloride. The similar compound,  $\text{C}_{26}\text{H}_{24}\text{O}_2\text{N}_2$ , obtained from tolualdehydecyanohydrin, melts at  $178^\circ$ , whilst the compound  $\text{C}_{24}\text{H}_{20}\text{O}_3\text{N}_2$ , prepared from benzylidene cyanohydrin and anisaldehyde, melts at  $224^\circ$ .

Incidentally it is stated that aldehydes yield somewhat unstable additive compounds with mercuric chloride; that obtained from benzaldehyde is a white, flocculent mass having the composition

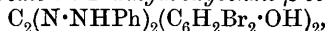


and is decomposed into its constituents by boiling water.

W. A. D.

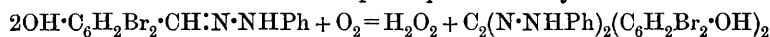
**Oxidation of *p*-Hydroxybenzaldehydephenylhydrazone and certain Derivatives to  $\alpha$ -Diketoneosazones.** By HEINRICH BILTZ and OTTO AMME (*Annalen*, 1902, 321, 1—32. Compare Abstr., 1899, i, 502, 910).—The process for preparing the aromatic  $\alpha$ -diketoneosazones by oxidising the corresponding phenylhydrazones in alcoholic solution with atmospheric oxygen does not succeed in the case of *p*-hydroxybenzaldehyde itself, although the reaction takes place quite readily with certain of its derivatives.

3 : 5 : 3' : 5'-Tetrabromo-4 : 4'-dihydroxybenzil- $\beta$ -osazone,



prepared by passing air through a dilute alcoholic potassium hydroxide solution of 3 : 5-dibromo-4-hydroxybenzaldehyde phenylhydrazone, crystallises from dilute alcohol in small, white leaflets melting at  $206^\circ$ . The reaction takes place at the ordinary summer temperature, but when the mixture is cooled to  $-6^\circ$  or  $-10^\circ$  the stereoisomeric  $\alpha$ -osazone is produced; this is also obtained in small, white leaflets, but it melts at  $144^\circ$ ; it is not converted into its isomeride by boiling with phenylhydrazine, nitrobenzene, or glacial acetic acid, although the transformation is effected by the agency of acetic anhydride, both oximes yielding the same triacetate, which crystallises in white prisms, melts at  $274$ — $275^\circ$ , and gives rise to the  $\beta$ -osazone on hydrolysis. The tetra-acetate results from the action of boiling acetic anhydride on the  $\alpha$ -osazone; it separates in yellowish-white leaflets, melts at  $161$ — $162^\circ$ , and is not obtained either from the  $\beta$ -osazone or the triacetate. The salicylosazones behave in a somewhat different manner on acetylation; when boiled for a short time with acetic anhydride, both stereoisomerides yield the same triacetyl derivative, which is triacetylsalicyl  $\beta$ -osazone, because it gives the  $\beta$ -osazone on hydrolysis; if, however, these osazones are heated with the anhydride in presence of sodium acetate, they both furnish the same tetra-acetate.

An oxidation of 3 : 5-dibromo-4-hydroxybenzaldehydephenylhydrazone with a definite volume of oxygen, either pure or atmospheric, showed that the reaction takes place quantitatively as follows :



theoretical yields are only obtained, however, when dilute alcohol is employed as solvent, pure water or absolute alcohol giving less satisfactory results.

3:5:3':5'-*Tetraiodo-4:4'-dihydroxybenzil-β-osazone*, obtained from 3:5-di-iodo-4-hydroxybenzaldehydephenylhydrazine (m. p. 157°) by the general method, crystallises from dilute alcohol in yellow leaflets and decomposes at 195°; the reaction takes place quantitatively in the manner indicated. The stereoisomeric *α-osazone* is produced when the experiment is performed at -5°; it crystallises from dilute alcohol with some difficulty and melts at 140—141°. The *triacetate* of the *β-osazone* represents the final product of the acetylation of this osazone, whereas the tetra-acetate is produced in any circumstance from the stereoisomeride; the former derivative crystallises in white leaflets melting at 270°, and the latter in yellow leaflets melting at 200°; both acetyl compounds yield the *β-osazone* on hydrolysis.

3:3'-*Dibromo-4:4'-dihydroxybenzil-osazone*, produced from 3-bromo-4-hydroxybenzaldehydephenylhydrazine (m. p. 105°), melts at 120° whilst still impure, and yields tarry products on treatment with the ordinary solvents; its *triacetate* crystallises in white, flexible, felted needles and melts at 164°.

*Vanillil-α-osazone*,  $C_2[C_6H_8(OH) \cdot OMe]_2(N_2HPh)_2$ , prepared by oxidising vanillinphenylhydrazine at -11° to -15°, is a yellow powder consisting of small leaflets melting at 155°; this substance is not transformed into the *β-isomeride* either by heating its solutions or by acetylation.

3:3'-*Dinitro-4:4'-dihydroxybenzil-osazone*, melting at 211°, is obtained by oxidising 3-nitro-4-hydroxybenzaldehydephenylhydrazine (m. p. 175°) at the ordinary temperature, and crystallises from nitrobenzene in rosettes of red prisms or lamellæ. When dissolved in alkali hydroxide solution and reprecipitated by acids, it becomes transformed into an *isomeride* melting at 130°; this substance, which is also formed as a direct product of oxidation, separates as a brownish-red, micro-crystalline powder, and is reconverted into the osazone of higher melting point by warming or agitating with glacial acetic acid. A third stereoisomeric *osazone* melting at 245° is obtained in certain cases, but the conditions which determine its formation have not been precisely defined; it separates from nitrobenzene in small, red crystals, and it forms a soluble potassium derivative from the solutions of which it is reprecipitated by the addition of acids. In this case, the oxidation of the hydrazine does not take place at -10°.

On acetylation, the osazone melting at 211° yields a *tetra-acetate* which gives rise to the osazone melting at 130° on alkaline hydrolysis; the latter isomeride merely furnishes a *triacetyl* derivative even by the action of acetic anhydride and sodium acetate, this product when hydrolysed regenerating the original osazone. The tetra- and tri-acetyl derivatives separate from the ordinary organic solvents in yellowish-brown crystals and melt respectively at 239° and 248°. The third osazone yields an acetyl compound melting at 305°.

G. T. M.

**Derivatives of 2-Methylcyclohexanone.** By LÉON TÉTRY (*Bull. Soc. Chim.*, 1902, [iii], 27, 302—307).—In the preparation of benzyl-

idene-2-methylcyclohexanone (compare Wallach, Abstr., 1896, i, 572), the author has succeeded in isolating a new substance which crystallises in long, colourless needles melting at  $152-153^{\circ}$ , and is probably 1- $\alpha$ -hydroxybenzyl-4-methylcyclohexanol-2; it yields a *diacetate* which crystallises in colourless needles soluble in ether or light petroleum, and melts at  $69-70^{\circ}$ .

By the oxidation of benzylidenemethylcyclohexanone with permanganate, benzoic and  $\beta$ -methyladipic acids are obtained, and by reduction with sodium amalgam, *benzylmethylcyclohexanone*, a mobile, colourless oil boiling at  $164^{\circ}$  under 11 mm. pressure. The latter substance yields an *oxime* which crystallises in slender, silky needles, melts at  $143^{\circ}$ , and is very soluble in ether, benzene, or alcohol, but less so in light petroleum.

By the reduction of dibenzylidene-2-methylcyclohexanone with sodium amalgam, the corresponding *dibenzylmethylcyclohexanone* is obtained; it forms colourless needles which melt at  $100^{\circ}$  and are soluble in ether or alcohol. Neither the dibenzylidene nor the dibenzyl compound reacts with hydroxylamine. A. F.

**3:5-Dinitroacetophenone and its Derivatives.** By LUDWIG BEREND and FRITZ HEYMANN (*J. pr. Chem.*, 1902, [ii], 65, 290—294).—3:5-Dinitrobenzoyl chloride crystallises from benzene in small, white needles, melts at  $74^{\circ}$ , and when treated with sodium and ethyl acetate yields *ethyl 3:5-dinitrobenzoylacetate*, which crystallises from alcohol in slender, bright yellow needles, or from ethyl acetate and light petroleum in long, compact prisms, and melts at  $92^{\circ}$ . The latter compound, when heated with 40 per cent. sulphuric acid for 8—10 hours, yields 3:5-dinitroacetophenone, which crystallises from light petroleum in lustrous needles, melts at  $82-84^{\circ}$ , and forms a *phenylhydrazone* melting at  $212^{\circ}$ . 3:5-Diaminoacetophenone crystallises from alcohol in bright yellow leaflets and melts at  $133-134^{\circ}$ .

3:5-Dinitrobenzoylacetone, obtained from acetylacetone in a similar manner, crystallises from alcohol in lustrous, yellowish needles and melts at  $153^{\circ}$ . R. H. P.

**Homologues of Deoxybenzoin.** By MARYA STRZELECKA (*Bull. Acad. Sci. Cracow*, 1902, 12—13).—Phenyl *p*-xylyl ketone,  $\text{COPh} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4\text{Me}$ ,

is formed when a mixture of the barium salts of *p*-tolylacetic and benzoic acids is distilled under 60 mm. pressure; it melts at  $57^{\circ}$ , whilst Strassmann (Abstr., 1889, i, 883) gives  $94^{\circ}$ . The *oxime* crystallises in slender needles melting at  $109^{\circ}$ .

With alcoholic potassium thiocyanate, *p*-xylyl bromide gives *p*-xylyl-thiocarbimide, which crystallises in white needles melting at  $134^{\circ}$ .

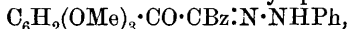
K. J. P. O.

**Synthesis of Hydroxyflavonole Derivatives.** By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1902, 35, 1679—1683).—By condensing phenoxyacetophenone,  $\text{COPh} \cdot \text{CH}_2 \cdot \text{OPh}$ , with metallic sodium, a compound,  $\text{C}_{16}\text{H}_{12}\text{O}_2$ , is obtained, which crystallises from alcohol in orange-coloured needles melting at  $120^{\circ}$ , and on reduction



yields a substance crystallising from alcohol in white needles melting at 118°.

The *phenylhydrazone* of 2:4:6-trimethoxydiphenyltriketone,



results from the action of benzenediazonium chloride on benzoyl-2:4:6-trimethoxyacetophenone, and crystallises from alcohol in plates melting at 137°. The *phenylhydrazones* of 2:4:6:4'-tetramethoxybenzoylacetophenone and 2:4:6:3'-tetramethoxy-4'-ethoxybenzoylacetophenone crystallise in leaflets melting respectively at 169° and 166—167°. These three phenylhydrazones dissolve in concentrated sulphuric acid to deep red solutions.

The *phenylhydrazone* of 2:4:6-trimethoxy-2'-ethoxybenzoylacetophenone forms orange-yellow needles and melts at 88—90°. G. T. M.

***β*-Ionone.** HAARMANN & REIMER (D.R.-P. 126959. Compare this vol., i, 342).—*β*-Ionone is readily obtained by heating *cyclocitral*-ideneacetoacetic acid (*β*-iononecarboxylic acid) at 220° in a current of carbon dioxide, distilling the residue in steam, and fractionating the oily distillate under diminished pressure, the fraction boiling at 135—145° being utilised as a source of the ketone. G. T. M.

**Acetylionone.** HAARMANN & REIMER (D.R.-P. 126960. Compare preceding abstract).—Acetyl-*ψ*-ionone (compare this vol., i, 342, 385), when heated under diminished pressure, becomes transformed into an isomeride melting at 121—122°, this product being of little use in the production of acetylionone. When, however, acetyl-*ψ*-ionone is treated at -10° with 80 per cent. sulphuric acid and the mixture subsequently heated at 50°, it undergoes transformation into *acetylionone*; this substance, which is obtained by diluting the product and distilling in steam, is a yellow oil, having an agreeable odour, boiling at 170—177° under 25 mm. pressure, and having a sp. gr. 1.03, and  $n_D$  1.521 at 18°. Ionone is produced from the acetyl derivative by hydrolysis with alkalis. G. T. M.

**Homologues of Ionone.** HAARMANN & REIMER (D.R.-P. 127424).—Citral and the homologues of acetone, when condensed with concentrated acids at low temperatures, furnish homologues of ionone, sulphuric acid giving rise to *β*-substituted ionones, whilst phosphoric or formic acid generally induces the formation of the corresponding *α*-derivatives.

*β*-Methylionone, obtained from citral and methyl ethyl ketone and 70 to 100 per cent. sulphuric acid at 0°, boils at 140—155° under 20 mm. pressure, and has a sp. gr. 0.935—0.938 at 20°; *α*-methylionone, produced by the aid of phosphoric acid at 30°, boils at 140—150° under 20 mm. pressure and has a sp. gr. 0.925—0.931 at 20°.

*β*-Dimethylionone, prepared from citral and methyl isopropyl ketone, boils at 155—160° under 20 mm. pressure, whilst the *α*-derivative boils at 150—155° under the same pressure. G. T. M.

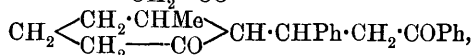
**Separation of Ianthone from Ionone.** HAARMANN & REIMER (D.R.-P. 127831).—Crude ianthone is treated with a slightly acid solution of sodium phenylhydrazine-*p*-sulphonate, the mixture being

subsequently rendered alkaline with sodium hydroxide and extracted with ether. Under these conditions, the ionone condenses with the hydrazine derivative to form a hydrazone soluble in sodium hydroxide, whilst the ianthone, which is not affected, is removed by the ether, and finally purified by distillation under diminished pressure. Ianthone is a pale yellow oil boiling at 162—172° under 15 mm. pressure and having a sp. gr. 0.943 and  $n_D$  1.5376 at 22°.

G. T. M.

**Semi-cyclic 1:5-Diketones.** By HANS STOBBE (*Ber.*, 1902, 35, 1445—1448).—The diketone,  $\begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{CH}_2 - \text{CO} \end{matrix} > \text{CH} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{COPh}$ , prepared from cyclopentanone and benzylideneacetophenone, crystallises from light petroleum in small prisms and melts at 78—80°. The *semi-carbazone*,  $\text{C}_{22}\text{H}_{26}\text{O}_2\text{N}_6$ , is insoluble in most solvents and melts and decomposes at 233°.

The diketone,  $\text{CHMe} < \begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{CH}_2 - \text{CO} \end{matrix} > \text{CHPh} \cdot \text{CH}_2 \cdot \text{COPh}$  or



from  $\beta$ -methylcyclohexanone and benzylideneacetophenone, crystallises from alcohol and melts at 149—151°. The *monoxime*,  $\text{C}_{22}\text{H}_{25}\text{NO}_2$ , crystallises from alcohol or benzene and melts at 215—216°.

T. M. L.

**Intramolecular Atomic Migrations. I and II.** By P. J. MONTAGNE (*Rec. Trav. Chim.*, 1902, [ii], 21, 6—29, 30—37).—I. The conversion of aromatic  $\alpha$ -diketones under the influence of alkalis into acids, as instanced in the change of benzil,  $\text{COPh} \cdot \text{COPh}$ , into benzoic acid,  $\text{OH} \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$ , has been studied with the object of determining whether the carbon atom of the wandering benzene nucleus, to which is attached the carbonyl group in benzil, also unites the phenyl group to the  $\alpha$ -carbon atom in benzoic acid. With alkalis, 4:4'-dichlorobenzil yields a dichlorobenzoic acid, which is oxidised to a 4:4'-dichlorobenzophenone; in the latter, the position of only one of the chlorine atoms is fixed. The following facts show that this substance is 4:4'-dichlorobenzophenone, and that the carbon atom which is linked to the carbonyl group in benzil is also attached to the  $\alpha$ -carbon atom in benzoic acid. The dichlorobenzophenone, on nitration, yields a dinitro-derivative identical with that obtained from the 4:4'-dichloro-3-nitrobenzophenone prepared from 4-chloro-3-nitrobenzoyl chloride and chlorobenzene; on reducing the mononitro-derivative, the corresponding 4:4'-dichloro-3-aminobenzophenone is formed, which, when oxidised, yields *p*-chlorobenzoic acid, the nucleus containing the amino-group being broken up. Thus the second chlorine atom in the dichlorobenzophenone, obtained from dichlorobenzoic acid, must be in the para-position relatively to the carbonyl group.

4:4'-Dichlorohydrobenzoin,  $\text{C}_2\text{H}_2(\text{C}_6\text{H}_4\text{Cl})_2(\text{OH})_2$ , prepared by reducing *p*-chlorobenzaldehyde with zinc and hydrochloric acid, crystallises in small, colourless needles melting at 151°, and on oxidation with dilute nitric acid gives 4:4'-dichlorobenzil, which crystallises in

long, yellow needles melting at  $200^{\circ}$ . 4:4'-Dichlorobenzilic acid,  $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\text{Cl})_2\cdot\text{CO}_2\text{H}$ , prepared from 4:4'-dichlorobenzil by the action of alcoholic potassium hydroxide, forms slender needles melting at  $101\cdot75^{\circ}$  and dissolves in sulphuric acid with a red coloration; the silver salt crystallises from benzene with  $1\text{C}_6\text{H}_6$  in colourless needles; the methyl ester forms white needles melting at  $60^{\circ}$ , and decomposes on heating into 4:4'-dichlorobenzophenone, carbon monoxide, and methyl alcohol. On oxidising dichlorobenzilic acid with chromic acid, 4:4'-dichlorobenzophenone (m. p.  $147\cdot75^{\circ}$  and b. p.  $353^{\circ}$  at 757 mm. pressure) was obtained (Dittrich, Abstr., 1891, i, 1237). 4:4'-Dichloro-3-nitrobenzophenone,  $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Cl}$ , prepared from 4-chloro-3-nitrobenzoyl chloride and chlorobenzene in the presence of aluminium chloride, crystallises in colourless needles melting at  $87^{\circ}$ . On nitrating dichlorobenzophenone or dichloronitrobenzophenone, 4:4'-dichlorodinitrobenzophenone is formed and melts at  $132\cdot5^{\circ}$ . On reducing the mononitro-derivative with stannous chloride, 4:4'-dichloro-3-aminobenzophenone is obtained, crystallising in yellow needles melting at  $140\cdot5^{\circ}$  and boiling at  $280^{\circ}$  under 11 mm. pressure; when oxidised by permanganate, *p*-chlorobenzoic acid is formed, and by the action of nitrous acid 4:4'-dichlorobenzophenone is produced.

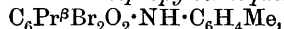
II. With the same object as that stated in the preceding section, the transformation of 4:4'-dichlorohydrobenzoin (an aromatic  $\alpha$ -glycol) into 4:4'-dichlorophenylacetaldehyde has been studied. The transformation is effected by heating the  $\alpha$ -glycol with excess of 35 per cent. sulphuric acid under pressure at  $150$ — $160^{\circ}$  for 36 hours; 4:4'-dichlorodiphenylacetaldehyde,  $\text{CH}(\text{C}_6\text{H}_4\text{Cl})_2\cdot\text{CHO}$ , thus obtained, forms crystals melting at  $149^{\circ}$ , and is oxidised by chromic acid to 4:4'-dichlorobenzophenone (*loc. cit.*).

The intermediate product,  $\text{C}_{14}\text{H}_{12}\text{O}$ , obtained in the transformation of hydrobenzoin into diphenylacetaldehyde, must, in consequence, have the formula  $\begin{array}{c} \text{CHPh} \\ \diagup \quad \diagdown \\ \text{CHPh} \end{array} > \text{O}$ , and not  $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CHPh} \\ \diagup \quad \diagdown \\ \text{CH}\cdot\text{OH} \end{array}$ .

K. J. P. O.

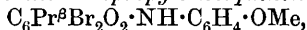
Reactions of the Dihalogen-thymoquinones. By O BÖTERS (*Ber.*, 1902, 35, 1502—1510. Compare Hoffmann, Abstr., 1901, i, 473).—The condensation between dibromothymoquinone and aniline or *p*-toluidine, involving the replacement of the methyl radicle by the arylamino-residue, takes place in a similar manner with *m*-toluidine and anisidine; dichlorothymoquinone is found to react in the same way.

3:6-Dibromo-5-*m*-toluidino-2-isopropylbenzoquinone,



crystallises from methyl alcohol in violet leaflets melting at  $171^{\circ}$ ; it is sparingly soluble in alcohol or benzene, dissolving more readily in acetone.

3:6-Dibromo-5-anisidino-2-isopropylbenzoquinone,

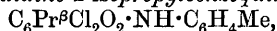


separates from alcohol in deep blue or violet needles which melt at  $196^{\circ}$ . The solution of these derivatives in concentrated sulphuric acid has a deep blue colour, and the compounds, when boiled with alcoholic sulphuric acid, are hydrolysed into 3:6-dibromo-5-hydroxy-2-isopropyl-

benzoquinone, which combines with *p*-toluidine in methyl alcohol solution to yield the corresponding salt,  $C_6Pr^{\beta}Br_2O_2 \cdot OH, C_6H_4Me \cdot NH_2$ , a substance separating in brick-red needles melting at  $150^{\circ}$ .

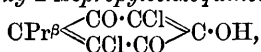
The *xylylidine* salt,  $C_6Pr^{\beta}Br_2O_2 \cdot OH, C_6H_3Me_2 \cdot NH_2$ , prepared in a similar manner, forms slender, deep violet needles melting at  $154^{\circ}$ .

3 : 6-Dichloro-5-*p*-toluidino-2-isopropylbenzoquinone,



produced by boiling together dichlorothymoquinone and *p*-toluidine in alcoholic solution, separates in deep violet leaflets and melts at  $187^{\circ}$ ; it is easily soluble in benzene, and only sparingly so in alcohol; its solution in concentrated sulphuric acid has a fine blue colour.

3 : 6-Dichloro-5-hydroxy-1-isopropylbenzoquinone,



obtained by boiling the preceding substance with alcoholic hydrogen chloride, separates from the cold solution in golden-yellow needles with a bronze reflex; it melts at  $126^{\circ}$  and is readily soluble in alcohol and solutions of the alkali hydroxides, carbonates, or hydrogen carbonates. The *silver* salt crystallises from dilute alcohol in white needles. The *methoxy*-derivative,  $C_6Pr^{\beta}Cl_2O_2 \cdot OMe$ , formed by the action of methyl iodide on the silver salt, crystallises from dilute alcohol in golden-yellow leaflets and melts at  $83-84^{\circ}$ .

The position of the substituent radicles in the basic molecule has an appreciable influence on the course of these condensations, for *o*-toluidine and *p*-xylylidine, which contain a methyl group in the ortho-position with respect to amidogen, give rise to diaminoquinones, the methyl group and one of the bromine atoms of dibromothymoquinone being simultaneously eliminated.

6-Bromo-3 : 5-di-*o*-toluidino-1-isopropylbenzoquinone,



which is obtained only in small yield, crystallises from alcohol in deep violet leaflets melting at  $131^{\circ}$ .

6-Bromo-3 : 5-di-*p*-xylylidino-1-isopropylbenzoquinone,



crystallises from alcohol in reddish-brown needles with a coppery lustre; it melts at  $166^{\circ}$  and dissolves in concentrated sulphuric acid to a brownish-violet solution.

When boiled with alcoholic sulphuric acid or hydrogen chloride, this compound undergoes a condensation whereby two mols. coalesce to form a substituted phenazine, two mols. of *p*-xylylidine being simultaneously eliminated. This reaction serves to establish the orientation of the radicles in the dixylylidinoquinone itself.

4 : 9-Dibromo-2 : 5 : 7 : 10-tetraoxy-1 : 6-di-*p*-xylyl-3 : 8-diisopropylphenazine,  $CPr^{\beta} \cdot CO \cdot C \cdot N(C_6H_3Me_2) \cdot C \cdot CO \cdot C \cdot Br$ , crystallises from absolute

alcohol in yellow needles melting at  $215^{\circ}$ ; its solution in concentrated sulphuric acid has a yellowish-brown colour. This substance is also produced by the action of alcoholic hydrogen bromide, but when hydrogen chloride is employed, the corresponding *dichlorophenazine* derivative is obtained; this compound, which has the same configuration as the preceding phenazine, contains the two chlorine atoms in the positions

4 and 9; it crystallises from a mixture of benzene and light petroleum in greenish-yellow needles melting at  $236^{\circ}$ .

The aliphatic amines behave differently towards dibromothymoquinone, this substance, when boiled with a methyl alcohol solution of methylamine, losing both its halogen radicles and becoming converted into 3:6-dimethylaminothymoquinone,  $C_6MePr^{\#}O_2(NHMe)_2$ , a compound crystallising in reddish-violet needles or plates melting at  $203^{\circ}$ , and dissolving in concentrated sulphuric acid to a yellow solution.

G. T. M.

**Dyeing with Mordants.** By CARL LIEBERMANN (*Ber.*, 1902, 35, 1490—1498).—Remarks suggested by a discourse delivered by Noelting on the theory of dyeing colouring matters on basic mordants.

The rule put forward by the author and Kostanecki, to connect the dyeing properties of hydroxyanthraquinone derivatives with their configuration, still applies generally to the other colouring matters of this type which have been subsequently discovered. According to this generalisation, the property of giving valuable colour lakes with the basic oxide mordants depends on the presence in the molecule of two hydroxyl groups or one carboxyl and one hydroxyl radicle in ortho-positions with respect to each other when one of the substituents is adjacent to the chromophoric residue.

The azo-compounds derived from diazotised anthranilic acid coupled with resorcinol and  $\beta$ -naphthol which dye wool mordanted with the basic oxides, probably owe this property to the presence of the carboxyl and hydroxyl radicles situated in ortho-positions with respect to the azo-group as indicated by the formulæ  $CO_2H \cdot C_6H_4 \cdot N:N \cdot C_6H_3(OH)_2$  and  $CO_2H \cdot C_6H_4 \cdot N:N \cdot C_{10}H_6 \cdot OH$ . Consequently these substances may be considered to follow the rule.

The author now divides colouring matters of this type into two classes. Firstly, those which rapidly give deep shades of colour with the ordinary mordanting oxides (aluminic and ferric oxides), and, secondly, the compounds which either do not dye with the ordinary basic mordants or at least only give very faint tints. The substances belonging to the second class may, however, give very good results with the oxides of the rarer metals.

The *o*-dihydroxy-compounds belong to the first class, whilst those derivatives containing the substituent radicles in other positions belong to the second. Anthrachrysone (1:3:5:7-tetrahydroxyanthraquinone) belongs to the second class, whilst hystazarin (2:3-dihydroxyanthraquinone) and quinizarin (*p*-dihydroxyanthraquinone) occupy an intermediate position, for even when carefully purified they produce moderately deep shades of colour on fabrics mordanted with ferric oxide or alumina. These three anthraquinone derivatives, however, all give better results with the rare oxides.

G. T. M.

**Conversion of Nitroanthraquinone Derivatives into Substituted Bromoaminoanthraquinones.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 128845).—1-Nitroanthraquinone and 1:8-dinitroanthraquinone, when heated at  $150^{\circ}$  with bromine and glacial acetic acid, become converted into *dibromo-1-aminoanthraquinone* and

tetrabromo-1 : 8-diaminoanthraquinone respectively ; these products are dark red powders insoluble in water, but soluble in alcohol, glacial acetic acid, xylene, nitrobenzene, or aniline to orange-coloured solutions.

*Dibromo-β-aminoanthraquinonesulphonic acid*, prepared by heating β-nitroanthraquinonesulphonic acid with concentrated hydrobromic acid, dissolves in water to an orange-coloured solution.

The properties of these compounds are tabulated. G. T. M.

**Derivatives of Nitroaminoanthraquinone.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 127780).—*Diacetyl-1 : 5-diaminoanthraquinone*, produced by acetylating 1 : 5-diaminoanthraquinone with acetic anhydride, separates in light brown, lustrous crystals, melts above 300°, and is converted into 4 : 8-dinitrodiacetyl-1 : 5-diaminoanthraquinone by the action of a mixture of concentrated nitric and sulphuric acids. The product is a yellow, crystalline powder, very sparingly soluble in the ordinary solvents but crystallising from benzene in brownish-yellow prisms. 4 : 8-Dinitro-1 : 5-diaminoanthraquinone, obtained in the form of its colourless *sulphate* by the action of concentrated sulphuric acid at 90° on the acetyl compound, crystallises from nitrobenzene in dark red leaflets with a green reflex ; the sulphate crystallises in flattened prisms.

4 : 5-Dinitrodiacetyl-1 : 8-diaminoanthraquinone, prepared in a similar manner to its isomeride, is a yellow, crystalline powder. When hydrolysed, it yields 4 : 5-dinitro-1 : 8-diaminoanthraquinone, a substance separating from pyridine or nitrobenzene in yellow crystals and giving rise to 1 : 4 : 5 : 8-tetra-aminoanthraquinone on reduction with sodium stannite. G. T. M.

**Dihalogen Derivatives of 1 : 5-Diaminoanthraquinonedisulphonic Acid.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 126393).—*Sodium dichloro-1 : 5-diaminoanthraquinonedisulphonate*, produced by adding sodium chlorate to a warm solution of sodium 1 : 5-diaminoanthraquinonedisulphonate in dilute sulphuric acid, separates from the mixture in yellowish-red needles on adding sodium chloride or hydroxide ; it dyes unmordanted wool in scarlet shades. The corresponding *dibromo-sulphonate* is obtained in a similar manner by substituting bromine dissolved in glacial acetic acid or dilute hydrochloric acid for the chlorate ; it crystallises from water in slender needles insoluble in the organic solvents. G. T. M.

**Introduction of Amino-radicles into 4-Nitro-1-hydroxyanthraquinone-2-sulphonic Acid.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 127438).—4-*p-Toluidino-1-hydroxyanthraquinone-2-sulphonic acid*,  $C_6H_4 \begin{matrix} \diagup CO \cdot C : C(OH) \\ \diagdown CO \cdot C : C(NHPh) \end{matrix} \begin{matrix} \diagup C \cdot SO_3H \\ \diagdown CH \end{matrix}$ , obtained by heating 4-nitro-1-

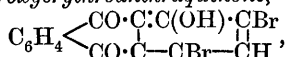
hydroxyanthraquinone-2-sulphonic acid with *p*-toluidine in 50 per cent. acetic acid, is sparingly soluble in water, dissolving either in this solvent or in alcohol to a blue solution. The corresponding *phenyl* and *α-naphthyl* compounds have similar properties ; they dissolve in concentrated sulphuric acid to yellow solutions, the addition of boric acid developing a green coloration. G. T. M.

**Bromo- $\beta$ -aminoalizarin.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 126603).— $\beta$ -Aminoalizarin cannot be brominated by bromine dissolved in glacial acetic or concentrated sulphuric acid, but *bromo- $\beta$ -aminoalizarin* is obtained when the reagent dissolved in a mixture of the two solvents is allowed to act at 150°. The product crystallises from glacial acetic acid in brown needles melting at 287°.

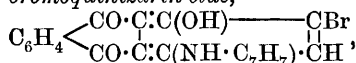
G. T. M.

[**Quinizarin Derivatives.**] FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 127532).—The halogen derivatives of quinizarin containing a halogen atom in the 2-position exchange this radicle for the residue R·NH— when heated with aromatic amines.

2 : 4-*Dibromo-1-hydroxyerythroanthraquinone*,



prepared by heating sodium hydroxyerythroanthraquinonesulphonate with bromine and water at 120—130°, crystallises in reddish-yellow needles and melts at 233°. When heated with *p*-toluidine at 80—100°, this substance loses the bromine atom in the 4-position and becomes converted into the *bromoquinizarin-blue*,



which crystallises in blue needles developing a green coloration with concentrated sulphuric acid.

G. T. M.

***p*-Halogen Derivatives of Hydroxyanthraquinones.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 127699. Compare preceding abstract).—*p*-*Dichloroanthrarufin*, prepared by passing chlorine into a glacial acetic acid solution of anthrarufin, separates in red needles having a metallic lustre; it is very sparingly soluble in solvents of low boiling point, but dissolves in nitrobenzene, separating in crystals having a red metallic lustre; its solution in a mixture of boric and sulphuric acids has a characteristic spectrum.

*p*-*Dichlorochrysazin*, produced either by direct chlorination in glacial acetic acid solution or by treatment with sodium chlorate and hydrochloric acid in a hot aqueous suspension, separates from nitrobenzene in crystals having a metallic lustre.

*p*-*Dibromoanthrarufin* is obtained by the action of potassium bromate and hydrobromic acid on a glacial acetic acid solution of anthrarufin; *p*-*dibromochrysazin* is prepared in a similar manner

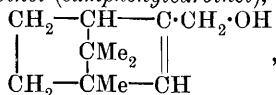
G. T. M.

**Monohydric Cyclic Alcohols.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 127855. Compare this vol., i, 102 and 299).—The cyclic glycols of the terpene series, when heated either alone or with dehydrating agents, yield unsaturated monohydric alcohols.

*Dehydromenthylcarbinol*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CHPr}^s \cdot \text{CH} \\ \text{CH}_2 \cdot \text{CHMe} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{OH} \end{array}$  distils from a boil-

ing mixture of *cis*-menthylglycol and 20 per cent. sulphuric acid as a limpid, highly refractive oil having an odour of anise; it boils at 99—101° under 18 mm. pressure. *Menthylcarbinol* is obtained on reducing the preceding compound with sodium and absolute alcohol; it is a colourless oil boiling at 85—90° under 20 mm. pressure.

*Dehydrocamphylcarbinol* (*camphenylcarbinol*),



is prepared by saturating the fused mixture of *cis*- and *trans*-camphanlyglycols or their solution in benzene with hydrogen chloride, the product being rendered alkaline with sodium hydroxide and distilled in steam; the carbinol distils over, whilst the unaltered *trans*-camphanlyglycol remains in the residue. The carbinol solidifies to a mass of colourless needles; it boils at 128—129° under 19 mm. pressure and has the odour of vanillin. *Camphanlycarbinol* results from the reduction of the preceding compound; it crystallises in colourless needles and melts at 62—64°. G. T. M.

**Syntheses in the Hydroaromatic Series by the Action of Zinc Chloride.** By IWAN L. KONDAKOFF [and, in part, E. LUTSCHININ] (*J. pr. Chem.*, 1902, [ii], 65, 201—233. See Abstr., 1900, i, 105).—A discussion of the formulæ of camphene, fenchene, fenchyl alcohol, &c., mainly polemical against G. Wagner.

The following new esters have been obtained by treating the corresponding hydrocarbon with a mixture of the acid and zinc chloride: *isoBornyl isobutyrate*, which is a colourless, viscous oil, boils at 132—133° under 19 mm. pressure, has a sp. gr. 0.9628 at 20°/20° and  $n_D$  1.46276, and is optically inactive. *isoBornyl isovalerate*, which boils at 132—133° under 13 mm. pressure, has a sp. gr. 0.9523 at 20°/20°,  $n_D$  1.46038, and  $[\alpha]_D + 47^\circ$  (the *isovaleric acid* used had  $[\alpha]_D + 2^\circ 8'$  at 20°). *isoFenchyl isovalerate*, which boils at 142—145° under 19 mm. pressure, has a sp. gr. 0.9437 at 20°/20°,  $n_D$  1.45749, and  $\alpha_D - 30'$  (the fenchene had  $[\alpha]_D + 6^\circ 55'$  and the *isovaleric acid*  $[\alpha]_D 2^\circ 8'$ ).

It is shown that commercial camphene and fenchene each contain two isomeric substances, one having the double linking in the side chain and the other in the ring. R. H. P.

**The Resin of Dammara Orientalis (Manila Copal).** By ALEXANDER TSCHIRCH and M. KOCH (*Arch. Pharm.*, 1902, 240, 202—229).—Two specimens of Manila copal were examined. The first was soluble in alcohol, comparatively soft, and with a dull surface. The resin melted at 115°; it had an acid number 134 determined by direct titration, 173 determined indirectly, saponification number 190, and iodine number 55.4. Succinic, formic, and acetic acids were detected amongst the products obtained by distilling the resin. Water extracted a minute quantity of a bitter substance. From a solution of the resin in ether, 1 per cent. aqueous ammonium carbonate extracted two acids. One of these, *mancopalic acid*,  $\text{C}_8\text{H}_{12}\text{O}_2$ , crystallised slowly from a solution of the two in a mixture of ethyl and methyl alcohols; it melts at 175° and has a specific rotation  $+56^\circ$ , an acid and saponification number 397, corresponding with monobasicity, and an iodine number 90.5, corresponding with a monoiodo-derivative; the *potassium* and *silver* salts were analysed; the acid contains no methoxyl groups, and does not react with phenylhydrazine. The second acid, *mancopalenic acid*,  $\text{C}_8\text{H}_{14}\text{O}_2$ , present in larger quantity, is amorphous; it melts at 100—105°, has an acid and saponification number 394, corre-



sponding with monobasicity, and an iodine number 90.9, corresponding with a monoiodo-derivative. From the remaining ethereal solution, 1 per cent. aqueous sodium carbonate extracted the closely related isomeric  $\alpha$ - and  $\beta$ -*mancopalolic* acids,  $C_{10}H_{18}O_2$ , which only differ in that the former melts at 85—100° and forms a lead salt which is insoluble in alcohol, whilst the second melts at 83—88° and forms a lead salt soluble in alcohol. Both have the acid and saponification number 326, corresponding with monobasicity, and the iodine number 74.5, corresponding with a monoiodo-derivative. The residue, when freed from ether and distilled with steam, yielded as a distillate an *essential oil* boiling at 165—170° and having a sp. gr. 0.849 at 15°, whilst there remained behind *mancopaloresen*,  $C_{20}H_{32}O$ , which is amorphous, melts at 80—85°, and is indifferent to alkalis. In 100 parts of the drug there were contained: *mancopalic* and *mancopalenic* acids, 4; *mancopalolic* acids, 75; *mancopaloresen*, 12; *essential oil*, 6; *water*, 2; other substances, 1.

The second specimen of Manila copal was partially soluble in alcohol, comparatively hard, and with a shining surface. It melted at 120°, had an acid number 118 by direct titration, 157 determined indirectly, a saponification number 165, and an iodine number 55.0. It contained no acids that could be extracted by ammonium carbonate from the ethereal solution; in other respects, it resembled the first sample, yielding the same *mancopalolic* acids and *mancopaloresen*. In 100 parts there were contained:  $\alpha$ - and  $\beta$ -*mancopalolic* acids, 80; *essential oil*, 5; *mancopaloresen*, 12; *water*, 2; other substances, 1.

The two samples appear to be derived from the same plant, and the results of the investigation confirm Wiesner's conclusion (*Rohstoffe des Pflanzenreiches*) that Manila copal is derived from one of the *Coniferae*, *Dammara orientalis*, and not from *Vateria indica*, one of the *Dipterocarpeæ*.

C. F. B.

**Constitution of Chitin.** By SIGMUND FRÄNKEL and AGNES KELLY (*Monatsh.*, 1902, 23, 123—132).—When chitin is treated with cold 70 per cent. sulphuric acid, the liquid gradually darkens and smells of acetone. After 2—3 days, the action is stopped by pouring into ice-water, and a series of decomposition products are obtained. Two of these have been investigated. *n*-Acetylglucosamine is easily soluble in water, with difficulty in methyl or ethyl alcohol, and insoluble in ether; it crystallises in long needles, melts with decomposition at about 190°, has a neutral reaction, and a strong reducing action on alkaline copper solutions; it does not form salts with acids, or a phenylhydrazine derivative. It has  $[\alpha]_D + 41.86^\circ$ , and is identical with Breuer's acetylglucosamine (*Abstr.*, 1898, i, 620). When boiled with sodium acetate and acetic anhydride, it does not form either of Lobry de Brun and Ekenstein's pentacetylglucosamines (*Abstr.*, 1899, i, 732).

The authors consider the other decomposition product to be *monoacetyldiglucoamine*,  $C_{14}H_{26}O_{10}N_2$ . It is easily soluble in water, the solution being dextrorotatory, does not reduce alkaline copper solutions, and gives no reaction with iodine or precipitate with neutral or basic lead acetate solution. It is not identical with Araki's chitosan (*Abstr.*,

1895, i, 444). The authors consider that the molecular formula of chitin is a multiple of  $C_{18}H_{30}O_{12}N_2$ . G. Y.

**Ononin.** By FRANZ VON HEMMELMAYR (*Monatsh.*, 1902, 23, 133—164. Compare Abstr., 1901, i, 160).—By crystallisation from alcohol, crude ononin, obtained from the ononis root, is separated into three fractions. The least soluble of these contains onon and ononin. *Onon*,  $C_{29}H_{38}O_{12}$ , is very slightly soluble in boiling water, alcohol or benzene, easily so in boiling glacial acetic acid and in pyridine, melts with decomposition at  $270^\circ$ , and with concentrated sulphuric acid and manganese dioxide forms a bright red liquid. Boiling baryta water has little action on it. When boiled with normal sulphuric acid, it yields an amorphous substance, which sinters at  $210^\circ$  and melts and decomposes at  $250^\circ$ , the filtrate reduces alkaline copper solutions, and with phenylhydrazine yields glucosazone.

Ononin is separated from onon by extraction with boiling water, from which it crystallises in colourless needles, which sinter at  $204^\circ$  and melt at  $210^\circ$ . With manganese dioxide and sulphuric acid, it forms a cherry-red, almost violet liquid. Heated with baryta water for 15 minutes, it yields onospin, prolonged heating giving ononetin. When heated at  $100^\circ$  with normal sulphuric acid, ononin yields dextrose, and Hlasiwetz's formylononetin,  $C_{19}H_{14}O_5$ , which is hydrolysed by baryta water to formic acid and ononetin. The ononetin obtained in this way shows the same behaviour as to its melting point as that from ononin and onospin, and consists of two isomerides. A methoxyl determination showed formylononetin to contain one methoxy-group. When boiled with acetic anhydride and sodium acetate, it yields a *monoacetyl* derivative, which is easily soluble in hot alcohol, chloroform or glacial acetic acid, and crystallises in stellate aggregates melting at  $164$ — $165^\circ$ . Ebullioscopic molecular weight determinations gave 293, 279.  $C_{21}H_{16}O_6$  requires 364.

The author considers that the correct formula for ononin is  $C_{25}H_{26}O_{11}$ , for onospin,  $C_{24}H_{26}O_{10}$ , for ononetin,  $C_{18}H_{16}O_5$ .

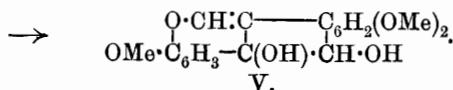
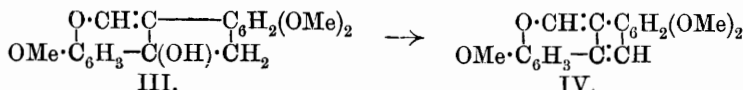
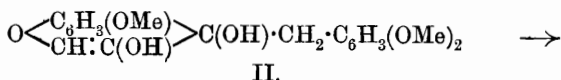
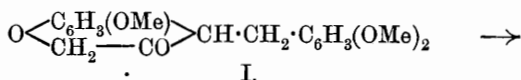
The middle fraction from the crude ononin consists of ononin in small quantity, and  $\psi$ -ononin. The latter, separated by further fractional crystallisation from alcohol, forms a white, indistinctly crystalline mass, which melts at  $206$ — $207^\circ$ , and gives a brown coloration with manganese dioxide and sulphuric acid. It is only moderately soluble in water or alcohol. When boiled with water, it is slowly converted, more quickly with baryta water, into  $\psi$ -onospin,  $C_{24}H_{24}O_{11}$ , which is easily soluble in hot water. From much water, it separates in a matted mass of delicate white needles, which contain  $2\frac{1}{2}H_2O$ , and melt at  $220$ — $221^\circ$ . From a concentrated aqueous solution, it separates in similar crystals, which melt at  $195$ — $197^\circ$ , and contain only a small percentage of water. Molecular weight determinations gave for the crystals of higher melting point 536, for those of lower melting point 518;  $C_{24}H_{24}O_{11}$  requires 488.

When boiled with dilute sulphuric acid,  $\psi$ -onospin is hydrolysed to dextrose and an amorphous substance. With acetic anhydride and sodium acetate, it forms a *tetra-acetyl* derivative, which melts at  $188$ — $189^\circ$ . With butyric anhydride and sodium butyrate, it forms

a *tetrabutryl* derivative melting at  $116^{\circ}$ . From the most soluble fraction from the crude ononin, there have been separated a glucoside melting at  $120$ — $130^{\circ}$ , and three substances melting respectively at about  $100^{\circ}$ ,  $220$ — $230^{\circ}$  and  $125$ — $130^{\circ}$ . G. Y.

**Brazilin.** By STANISLAUS VON KOSTANECKI and V. LAMPE (*Ber.*, 1902, **38**, 1667—1674. Compare *Abstr.*, 1899, i, 538, and Gilbody, Perkin, and Yates, *Trans.*, 1901, **79**, 1396).—The formula for trimethylbrazilin suggested by Feuerstein and Kostanecki readily accounts for the formation of 2-carboxy 5-methoxyphenoxyacetic acid on oxidation, providing that it is written in its tautomeric form,  $\text{O} \langle \text{C}_6\text{H}_3(\text{OMe}) \rangle \text{CH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_3(\text{OMe})_2$ . This ether, which is readily obtained by methylating brazilin with methyl sulphate in a boiling solution of potassium hydroxide, yields the crystalline acetyl derivative melting at  $174$ — $176^{\circ}$  when heated with acetic anhydride. The trimethyl ether on oxidation with cold chromic acid, yields a substance,  $\text{C}_{19}\text{H}_{16}\text{O}_6$ , separating from alcohol or benzene in colourless, acicular crystals decomposing at  $165^{\circ}$ . In spite of the difference in properties, this product is considered to be identical with trimethylbrazilone described by Gilbody and Perkin as crystallising in yellow needles and melting at  $191^{\circ}$ . The acetyl derivative of trimethylbrazilin on oxidation with cold chromic acid yields a compound,  $\text{C}_{19}\text{H}_{16}\text{O}_6$ , recently described by Herzig and Pollok as  $\beta$ -trimethylbrazilone (compare this vol., i, 483).

The trimethylbrazilone, obtained from trimethylbrazilin, behaves like a glycol rather than a ketone, and when heated above its melting point loses water, yielding dehydrotrimethylbrazilone,  $\text{C}_{19}\text{H}_{16}\text{O}_5$ . This series of changes can be explained by Feuerstein and Kostanecki's formula on the assumption that during oxidation rearrangement occurs in such a manner that a new central ring is produced.



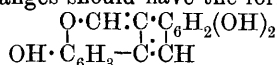
The last formula represents trimethylbrazilone, whilst the fourth indicates the product of its dehydration.

Acetyltrimethyldehydrobrazilone (m. p.  $176^{\circ}$ ), already studied by

Herzig and by Gilbody and Perkin, when reduced with fuming hydriodic acid, loses its methyl and acetyl groups and becomes converted into a *compound*,  $C_{16}H_{10}O_5$ , which crystallises in needles containing  $1H_2O$  and decomposing indefinitely between  $250^\circ$  and  $315^\circ$ ; this substance dissolves in sodium hydroxide to a colourless solution which absorbs oxygen and becomes brownish-red; the alcoholic solution develops a green coloration with ferric chloride. With acetic anhydride and sodium acetate, the reduction product yields a *tetra-acetyl* derivative crystallising from glacial acetic acid in white needles melting at  $239-240^\circ$ .

The following modified formula, 
$$\begin{array}{c} O \cdot CH : C - C_6H_2(OMe)_2 \\ OMe \cdot C_6H_3 - CH \cdot CH \cdot OH \end{array}$$
 for trimethylbrazilin is now suggested, which indicates the formation of the new ring. G. T. M.

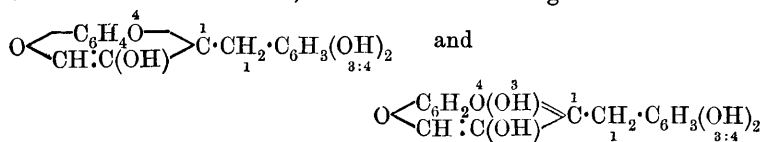
**Brazilin.** By E. BOLLINA, STANISLAUS VON KOSTANECKI, and JOSEF TAMBOR (*Ber.*, 1902, 35, 1675—1678. Compare preceding abstract).—The oxidation product of trimethylbrazilin (trimethylbrazilone), when heated with fuming hydriodic acid, loses its methyl radicles and becomes simultaneously dehydrated and reduced; the product formed as a result of these changes should have the formula



(compare with formulæ IV and V in preceding abstract); the *compound*  $C_{16}H_{10}O_4$  is obtained from dilute alcohol in grey leaflets melting at  $350^\circ$ ; its solution in sodium hydroxide is colourless with a blue fluorescence and the alcoholic solution develops, with ferric chloride, a blue coloration which changes to green. The *triacetyl* derivative, obtained by the action of sodium acetate and acetic anhydride, crystallises in white needles and melts at  $245^\circ$ .

Trimethylbrazilone, on treatment with cold nitric acid of sp. gr. 1.3, changes quantitatively into a *compound*,  $C_{19}H_{19}O_9N$ , which crystallises from glacial acetic acid and alcohol in yellow needles melting at  $225^\circ$ . The solution of this substance in dilute alkali hydroxide solution has a deep purple colour and when gently warmed yields *p*-methoxysalicylic acid and two neutral *compounds* melting at  $122^\circ$  and  $206^\circ$ , the acidic substance being the principal product.

The communication concludes with a discussion of the constitutions of brazilein and hæmatein, for which the following formulæ



are respectively suggested.

G. T. M.

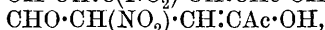
**Brazilin and Hæmatoxylin.** Part VII. By JOSEF HERZIG and JACQUES POLLAK (*Monatsh.*, 1902, 23, 165—179. Compare Abstr., 1901, i, 478)—Simultaneous reduction and acetylation of brazelein

leads to a *triacetyl* derivative,  $C_{16}H_9O(OAc)_3$ , which crystallises from alcohol, ethyl acetate, or acetic acid in white, glistening leaflets which darken at  $170^\circ$  and melt at  $190-195^\circ$ . Attempts to further acetylate, or to reduce and acetylate, it were without success. When hydrolysed with alkalis, it forms a red solution from which an amorphous substance is precipitated by addition of acid. On hydrolysis with sulphuric acid in acetic acid solution, a crystalline substance separates having the composition of an additive product of brazilein and sulphuric acid  $C_{16}H_{12}O_5 \cdot H_2SO_4$ . An additive product,  $C_{16}H_{12}O_5 \cdot HCl$ , is formed by treating brazilein with hydrogen chloride in presence of alcohol. With acetic anhydride, sodium acetate, and zinc dust, it yields a product apparently identical with the triacetyl derivative. The oxidation of acetyltrimethylbrazilin yields a substance having the composition of trimethylbrazilin and not of acetyltrimethyldehydrobrazilin (compare Abstr., 1896, i, 379); this product forms colourless crystals which decompose at  $150-160^\circ$  and at  $160-170^\circ$  resolidify to trimethyldehydrobrazilin. As Gilbody and Perkin (Proc., 1899, 15, 27) find trimethylbrazilone to form straw coloured needles melting at  $191^\circ$ , the authors term their product  *$\beta$ -trimethylbrazilone*. It is also formed by the oxidation of trimethylbrazilin. From the solution of  *$\beta$ -trimethylbrazilone* in warm alkali, acids precipitate a substance melting at  $193-195^\circ$ , which on acetylation yields acetyltrimethyldehydrobrazilin and is therefore probably trimethyldehydrobrazilin. Acetylation of  *$\beta$ -trimethylbrazilone* yields acetyltrimethyldehydrobrazilin. Reduction as also reduction and acetylation lead to an amorphous product.

*Acetyl- $\beta$ -trimethyldehydrobrazilin*,  $C_{16}H_9O(OMe)_3 \cdot OAc$ , formed by acetylation of the product of the action of concentrated sulphuric acid and alcohol on  *$\beta$ -trimethylbrazilone*, melts at  $183-185^\circ$ . With potassium hydroxide and methyl iodide, it yields  *$\beta$ -tetramethyldehydrobrazilin*, which melts at  $156-159^\circ$ .

*$\alpha$ -Tetramethyldehydrobrazilin* is formed by the action of potassium hydroxide and methyl iodide on acetyl- *$\alpha$ -trimethyldehydrobrazilin*; it melts at  $163-165^\circ$ . The action of potassium hydroxide and methyl iodide on  *$\beta$ -trimethylbrazilone* yields  *$\alpha$ -* and  *$\gamma$ -tetramethyldehydrobrazilins*, which melt at  $130-135^\circ$ . G. Y.

**Nitration of Furfuran and a Derivative of Nitrosuccinaldehyde.** By R. MARQUIS (*Compt. rend.*, 1902, 134, 776-777).—The thick, unstable, non-crystallisable, and non-volatile liquid obtained by the action of nitric acid on furfuran (Abstr., 1901, i, 222) readily reduces Fehling's solution and ammoniacal silver nitrate in the cold and forms a crystalline phenylhydrazone. It seems to be a *nitrosuccinaldehyde monoacetin*,  $OH \cdot CH : C(NO_2) \cdot CH : CAc \cdot OH$  or

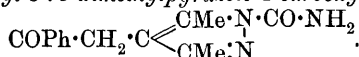


and this view is confirmed by analysis and cryoscopic determinations. When boiled with water, it loses nitrogen oxides and yields an aldehyde which forms a hydrazone containing no oxygen. In the nitration of furfuran in the presence of acetic anhydride, the nucleus is broken and nitrosuccinaldehyde monoacetin is formed, but on treatment with

pyridine (*loc. cit.*), the nucleus is again closed with production of nitro-furfuran ( $\text{NO}_2 = 3$  or 4). C. H. B.

**Benzoyldiacetylene and Acetylmethylfurfuran.** By FR. MARCH (*Compt. rend.*, 1902, 134, 843—845. Compare Abstr., 1901, i, 596).—The triketone, benzoyldiacetylene, and hydroxylamine yield 4-phenacyl-3:5-dimethylisooxazole,  $\text{COPh} \cdot \text{CH}_2 \cdot \text{C} \begin{smallmatrix} \text{CMe} \cdot \text{O} \\ \text{CMe} \cdot \text{N} \end{smallmatrix}$ , which crystallises in slender needles melting at  $124\text{--}125^\circ$ ; when the triketone is treated with excess of hydroxylamine, the *oxime* of the *isooxazole* is produced; it crystallises well and melts at  $131^\circ$ .

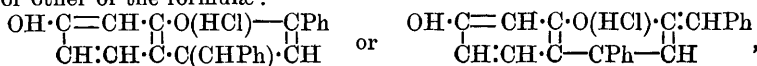
The compound (m. p.  $87\text{--}88^\circ$ ) obtained by the action of phenylhydrazine on the triketone is now shown to be 1-phenyl-4-phenacyl-3:5-dimethylpyrazole,  $\text{COPh} \cdot \text{CH}_2 \cdot \text{C} \begin{smallmatrix} \text{CMe} \cdot \text{NPh} \\ \text{CMe} \cdot \text{N} \end{smallmatrix}$ , whilst the compound (m. p.  $262\text{--}264^\circ$ ) produced by the action of semicarbazide on the triketone is 4-phenacyl-3:5-dimethylpyrazole-1-carboxylamide,



With ammonia, the triketone yields 4-acetyl-2-phenyl-5-methylpyrrole,  $\text{NH} \begin{smallmatrix} \text{CMe} \cdot \text{C} \cdot \text{COMe} \\ \text{CPh} \cdot \text{CH} \end{smallmatrix}$ , which crystallises in slender needles melting at  $177\text{--}178^\circ$ .

By the action of zinc chloride on a solution of the triketone in acetic acid, or, better, by distilling the triketone under reduced pressure, 4-acetyl-2-phenyl-5-methylfurfuran,  $\text{O} \begin{smallmatrix} \text{CMe} \cdot \text{C} \cdot \text{COMe} \\ \text{CPh} \cdot \text{CH} \end{smallmatrix}$ , is formed, and crystallises in needles melting at  $56\text{--}57^\circ$ , and boils at  $179^\circ$  under 18 mm. pressure; the *semicarbazone* melts at  $251\text{--}252^\circ$ , the *oxime* at  $111\text{--}112^\circ$ . The last-mentioned substance undergoes the Beckmann transformation under the action of phosphorus pentachloride, yielding an *amide*,  $\text{O} \begin{smallmatrix} \text{CMe} \cdot \text{C} \cdot \text{CO} \cdot \text{NHMe} \\ \text{CPh} \cdot \text{CH} \end{smallmatrix}$ , which melts at  $146\text{--}148^\circ$ . K. J. P. O.

**Condensation Product from Phenylacetylacetophenone and Resorcinol.** By CARL BÜLOW and HANS GROTOWSKY (*Ber.*, 1902, 35, 1519—1528. Compare Abstr., 1901, i, 400, 559, 603, and this vol., i, 112, 113).—7-Hydroxy-2-phenyl-4-benzylidene-1:4-benzopyranol hydrochloride, produced by passing hydrogen chloride into a glacial acetic acid solution of phenylacetylacetophenone and resorcinol, crystallises from a mixture of alcohol and hydrochloric acid in yellowish-red needles containing  $2\text{H}_2\text{O}$ . The substance may be represented by one or other of the formulæ:



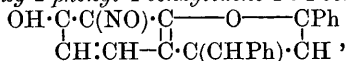
the former being the more probable.

The free *pyranol* could not be obtained crystalline; the *picrate* is insoluble in the ordinary organic solvents and decomposes at  $208^\circ$ .

The *acetyl* derivative of the pyranol, obtained by the action of acetic anhydride and sodium acetate, is soluble in the ordinary organic solvents, crystallises in yellow needles, and melts at 125—127°. The corresponding *benzoyl* derivative,  $C_{22}H_{15}O \cdot OBz$ , separates from alcohol in greenish-yellow needles and melts at 189°.

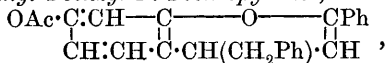
*7-Methoxy-2-phenyl-4-benzylidene-1:4-benzopyranol*, prepared by the action of sodium methoxide and methyl iodide on the pyranol hydrochloride, crystallises from alcohol in yellow needles melting at 107—108.5°.

*8-Nitroso-7-hydroxy-2-phenyl-4-benzylidene-1:4-benzopyranol*,



obtained by treating the pyranol hydrochloride with a cold aqueous solution of sodium nitrite, is a red powder soluble in most organic solvents except light petroleum; it decomposes at 172°. All the preceding compounds except the last exhibit a green fluorescence when dissolved in concentrated sulphuric acid.

*7-Acetoxy-2-phenyl-4-benzyl-1:4-benzopyranol*,



produced by reducing 7-acetoxy-2-phenyl-4-benzylidene-1:4-benzopyranol with zinc dust and a mixture of acetic acid and its anhydride, is a white, amorphous substance which sinters at 60° and melts indefinitely at high temperatures.

The pyranol hydrochloride, when heated with a strong solution of sodium hydroxide, yields a mixture of acetophenone, and  $\omega$ -phenylres-acetophenone, together with traces of resorcinol and benzoic acid. This hydrolysis is evidence in favour of the first formula suggested for the pyranol.

G. T. M.

**Action of Caro's Reagent on Alkaloids.** By E. SPRINGER (*Chem. Centr.*, 1902, i, 761—762; from *Pharm. Zeit.*, 47, 157).—The results of experiments on the behaviour of alkaloids with Caro's reagent (compare Abstr., 1900, i, 133) and also with a mixture of a 5 per cent. aqueous solution of hydrogen peroxide with five times its weight of concentrated sulphuric acid (compare Abstr., 1900, i, 206) show that neither of these reagents furnishes a characteristic test for individual alkaloids, brucine being the only one which gave a very distinct and characteristic coloration. The use of colloidal platinum as recommended by Bredig also failed to produce more intense colorations. Caro's reagent appeared to be a stronger oxidising agent than hydrogen peroxide and sulphuric acid.

E. W. W.

**Caffeine Iodides.** By A. FAUCON (*J. Pharm. Chim.*, 1902, [vi], 15, 370—373).—'Caffeine iodide' (hydriodide of tetraiodocaffeine) is a very unstable compound and always contains a considerable proportion of free iodine.

H. R. LE S.

**Acyl Derivatives of the Cinchona Alkaloids.** VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 128116. Compare Abstr., 1901, i, 738, 739).—The acyl derivatives of the cinchona alkaloids

may be readily obtained by heating these bases with the aryl esters of the organic acids either alone or in a suitable solvent.

Acetylquinine results from the interaction of quinine and phenyl acetate at 120—130°; the benzoyl derivative is obtained by the agency of phenyl benzoate.

Quinine ethyl carbonate is produced from the alkaloid by heating it with phenyl ethyl carbonate. *Quininecarbamide*,  $C_{20}H_{23}ON_2 \cdot CO \cdot NH_2$ , prepared by the action of phenyl carbamate, separates from dilute alcohol in colourless crystals and melts at 210°.

*Salicyllylquinine*,  $C_{20}H_{23}ON_2 \cdot CO_2 \cdot C_6H_4 \cdot OH$ , prepared by the interaction of the alkaloid and salol, separates from dilute alcohol in colourless crystals melting at 140°. *Salicyllylquinidine*, produced in a similar manner, is isolated in the form of its *salicylate*, a salt crystallising from alcohol in white needles melting at 168°.

*Cinnamylquinine*,  $C_{20}H_{23}ON_2 \cdot CO_2 \cdot CH : CHPh$ , obtained by the action of phenyl cinnamate, crystallises from ether in slender, white needles and melts at 111°. *Succinylquinine*,  $C_2H_4(CO_2 \cdot C_{20}H_{23}ON_2)_2$ , produced in a similar manner, is readily soluble in most organic solvents and crystallises in needles melting at 97°. G. T. M.

**Benzoyllupinine.** EMANUEL MERCK (D.R.-P. 129561).—*Benzoyllupinine*,  $C_{10}H_{18}ONBz$ , obtained either by heating lupinine with benzoyl chloride or benzoic anhydride or by subjecting the base to the Schotten-Baumann reaction, crystallises from dilute alcohol in colourless needles melting at 48—49°, and is extremely soluble in the ordinary organic solvents but does not dissolve in water.

The *hydrochloride* separates in colourless leaflets which are very soluble in water or alcohol; it melts at 208°. G. T. M.

**Detection of Lysin and Ornithin.** By R. O. HERZOG (*Zeit. physiol. Chem.*, 1902, 34, 525—527).—Lysin and ornithin readily form additive products with phenylthiocarbamide, but as these do not crystallise at all well, they are not of much value for the detection of the bases. On treatment with concentrated hydrochloric acid, the additive products yield hydantoins, which crystallise remarkably well.

The product from lysin,  $NHPh \cdot CO \cdot NH \cdot [CH_2]_4 \cdot CH \begin{smallmatrix} NH \cdot CO \\ | \\ CO \cdot NPh \end{smallmatrix}$ , crystallises from a mixture of alcohol and acetone and melts at 183—184°. The corresponding compound from ornithin melts at 191—192°.

J. J. S.

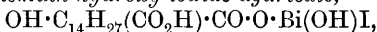
**Substances contained in Plants.** By PAUL SIEDLER (*Chem. Centr.*, 1902, i, 823; from *Ber. Pharm. Ges.*, 12, 64—84).—[With KÖRNER.]—0.04 per cent. of *tanacetine-Riedel*, has been isolated from the flowers of *Tanacetum vulgare*. This alkaloid or mixture of alkaloids forms a viscous, oily liquid, has a bitter, burning taste, is very slightly soluble in water, but readily so in alcohol or ether, is very volatile in steam, and combines with inorganic acids to form very hygroscopic salts.

The roots of *Cynoglossum officinale* yield 0.12 per cent. of an



alkaloid *cynoglossine-Riedel*, which, when freshly prepared, forms a clear, viscous liquid, has an extremely bitter taste, and a distinct narcotic odour similar to that of pelletierine, is rather soluble in water, soluble in all proportions of ether, alcohol, or chloroform, and forms well characterised salts with mineral acids. According to Kobert, tanacetine and cynoglossine have only very weak physiological action.

[With WINZHEIMER.]—Agaricic acid (compare Jahns, Abstr., 1884, 353; Schmieder, *Arch. Pharm.*, 1886, 224, 641) crystallises with  $1\frac{1}{2}\text{H}_2\text{O}$ , is only very slightly decomposed at  $100^\circ$ , and forms clear solutions in alkali carbonates. The normal salts are readily soluble in water, forming faintly alkaline solutions which only become clear, however, on the addition of a small excess of alkali. Attempts to decompose the normal salt with elimination of water by heating above  $120^\circ$ , according to Jahns' and Schmieder's method, failed. Sodium hydrogen agaricate softens at  $160^\circ$  and decomposes and melts about  $180^\circ$ , whilst the potassium salt melts at  $200^\circ$  without previously softening. The carboxyl groups of the acid do not appear to have equal values. The *normal* and *basic bismuth* salts,  $\text{Bi}_2\text{C}_{43}\text{H}_{84}\text{O}_{15}$ ,  $\text{BiC}_{16}\text{H}_{29}\text{O}_6$ , and  $\text{BiC}_{16}\text{H}_{29}\text{O}_6\cdot\text{BiO}\cdot\text{OH}$ , resist the action of dilute acids to an extraordinary extent, and have an astringent action. *Bismuth diagaricate monotannate*,  $\text{BiC}_{30}\text{H}_{37}\text{O}_{14}$ , *basic bismuth agaricate tannate*,  $\text{Bi}_2\text{C}_{44}\text{H}_{46}\text{O}_{24}$ , and *bismuth monoagaricate ditannate*,  $\text{Bi}_2\text{C}_{72}\text{H}_{64}\text{O}_{41}$ , have similar physiological effects. *Bismuth hydroxy-iodide agaricate*,



is a pale grey powder corresponding with airol. Diethyl agaricate and dimethyl agaricate melt at  $36\text{--}37^\circ$  and  $62\text{--}62.5^\circ$  respectively. Acetylagic acid melts at  $81^\circ$ . When agaricic acid is heated at  $140\text{--}160^\circ$ , a sand coloured compound melting at  $30^\circ$  is formed; the composition of this substance does not agree with that of an anhydride. *Agaricic diphenetide*,  $\text{OH}\cdot\text{C}_{14}\text{H}_{27}(\text{CO}\cdot\text{C}_8\text{H}_{10}\text{ON})_2$ , and *agaricic monophenetide*,  $\text{OH}\cdot\text{C}_{14}\text{H}_{27}(\text{CO}_2\text{H})\cdot\text{CO}\cdot\text{C}_8\text{H}_{10}\text{ON}$ , are prepared by condensing the acid with *p*-phenetidine at  $140\text{--}160^\circ$ . The former is a bluish-white, crystalline powder, melts at  $151^\circ$ , and is only slightly soluble in organic solvents, whilst the latter is an almost colourless, crystalline powder, contains water, and is readily soluble in organic solvents; the anhydrous salt melts at  $100^\circ$ . Different products are obtained when the condensation with *p*-phenetidine is effected at  $200^\circ$ .

Körner has found that the proportions of emetine, cephaline and psychotrine (compare Paul and Cownley, *Amer. J. Pharm.*, 73, Nos. 1, 2, 3) contained in Rio ipecacuanha bark are as 1:0.5:0.1 respectively, and in Carthagen bark 1:1:0.2. E. W. W.

**Methylenedipiperidine.** By ERNST SCHMIDT (*Arch. Pharm.*, 1902, 240, 230—231).—An introduction to the paper with which the following abstract deals. C. F. B.

**Methylenepiperidines of Various Origin.** By PAUL KOHLER (*Arch. Pharm.*, 1902, 240, 231—240).—Methylenedipiperidine,  $\text{CH}_2(\text{C}_5\text{NH}_{10})_2$ , was prepared by warming piperidine with trioxymethylene (Ehrenberg, Abstr., 1887, 1026); by treating piperidine with methylene iodide, or

boiling it with methylene chloride, in alcoholic solution (Trebst, *Inaug. Diss. Jena*, 1890); and by mixing piperidine with aqueous sodium hydroxymethylsulphonate (formaldehyde sodium hydrogen sulphite; Kraut, *Abstr.*, 1890, 1092). An identical product is obtained in all cases, boiling at 230—231° and having a sp. gr. 0.920—0.921 at 15°.

Methylenedipiperidine is a diacid base, but its salts are very unstable, decomposing with formation of piperidine salts. By neutralising it in alcoholic solution with hydrogen chloride and allowing the solution to evaporate in a desiccator, a mixture of its chloride with that of piperidine was apparently obtained; the *aurichloride* forms a flocculent precipitate and melts at 210—214°. A platinichloride could not be obtained. When treated with methyl iodide in alcoholic solution, methylenedipiperidine forms the *monohydriodide*, which melts at 125°, and methylpiperidine methiodide,  $C_5NH_{10}Me, MeI$  (the *aurichloride* corresponding with which melts at 278°), together with piperidine hydriodide.

C. F. B.

**Preparation of *n*-Methylgranatanine by the Electrolytic Reduction of *n*-Methylgranatonine.** By ANTONIO PICCININI (*Gazzetta*, 1902, 32, i, 260—265).—When electrolysed in dilute sulphuric acid solution, *n*-methylgranatonine is converted almost quantitatively into *n*-methylgranatanine, no intermediate products being apparently formed. The reduction may also be effected by means of zinc dust and dilute sulphuric acid.

T. H. P.

[Electrolytic Reduction of Pyrroles.] MAXIMILIANO DENNSTEDT (D.R.-P. 127086).—The reduction of pyrrole and its homologues to the corresponding dihydro-derivatives is readily effected by suspending the substance in dilute sulphuric acid contained in the cathode cell of an electrolytic apparatus, the cathode being of lead and the current having a density of 1 ampere per sq. cm.

In this manner, pyrrole readily yields dihydropyrrole, and ethylpyrrole gives rise to dihydroethylpyrrole, the platinichloride,  $(C_6H_{11}N)_2, H_2PtCl_6$ , of which forms yellow needles melting at 170°. Diethylpyrrole may be similarly reduced.

G. T. M.

**Studies in the Furfuran and Pyrrole Groups. I.** By FRANZ FEIST (*Ber.*, 1902, 35, 1537—1544).—A discussion of the various syntheses of furfuran- and pyrrole-carboxylic acids and of the author's own results, which are detailed in the following three abstracts.

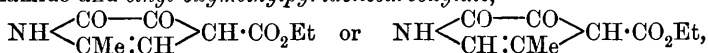
R. H. P.

**Studies in the Furfuran and Pyrrole Groups. II. Condensation of Esters of  $\beta$ -Ketonic Acids with Chloroacetone and Ammonia.** By FRANZ FEIST [and, in part, B. WIDMER and R. DUBUSCH] (*Ber.*, 1902, 35, 1545—1556).—The condensation of ethyl acetoacetate with chloroacetone and ammonia yields, in addition to ethyl 2:5-dimethylpyrrole-3-carboxylate (Hantzsch, *Abstr.*, 1890, 1155), *ethyl 2:4-dimethylfurfuran-3-carboxylate*, which is an oil boiling at 97° under 10 mm. pressure, and is always obtained contaminated with

another compound,  $C_7H_{14}O_4$  (?); the latter is either a diketone or ketone-alcohol and crystallises in lustrous leaflets melting at  $80^\circ$ . The analogous condensation with aniline yields *ethyl 1-phenyl-2:5-dimethylpyrrole-3-carboxylate*; this distils at  $225^\circ$  under 40 mm. pressure, and when cold solidifies to white crystals melting at  $43^\circ$ ; it is soluble in organic solvents, and when hydrolysed yields the corresponding *acid*, which crystallises from alcohol and melts and decomposes at  $205^\circ$ .

The *barium*, *silver*, *silver hydrogen*, and *silver ethyl* salts of 3-carboxy-2-methylfurfuran-4-acetic acid (Abstr., 1899, i, 675) are described; this acid, when boiled with water, yields 2:4-dimethylfurfuran-3-carboxylic acid, which forms crystalline *barium* (with  $6H_2O$ ), *calcium* (with  $4H_2O$ ), and *silver* salts, and oily *methyl* and *ethyl* esters.

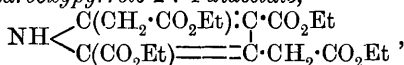
When ammonia is passed into an ethereal solution of ethyl oxalacetate and chloroacetone, condensation ensues with the formation of oxamide and *ethyl oxymethylpyridonecarboxylate*,



which dissolves in alkalis, is insoluble in alcohol, melts at  $223^\circ$ , and can be sublimed. The corresponding *acid* crystallises in lustrous, white leaflets (with  $2H_2O$ ), melts and decomposes, when anhydrous, at  $255^\circ$ , and forms *potassium* (decomposing at  $283^\circ$ ), *barium*, and *silver* salts. The *amide* is a white powder, soluble in ammonia, and decomposes above  $280^\circ$ . The acid, when heated above its melting point, evolves carbon dioxide and forms *oxymethylpyridone*,  $C_6H_7O_2N$ , which sublimes in small needles, melts at  $201\text{--}202^\circ$ , is soluble in sodium carbonate, and reduces alkaline permanganate and ammoniacal silver oxide solutions. All these pyridone compounds give a green (or greenish-blue) coloration with ferric chloride. R. H. P.

Studies in the Pyrrole Group. III. Condensation of Esters of *iso*Nitroso- $\beta$ -ketonic Acids with Esters of  $\beta$ -Ketonic Acids by Reduction. By FRANZ FEIST (*Ber.*, 1902, 35, 1556—1557).—

*Ethyl 3:5-dicarboxypyrrole-2:4-diacetate*,



obtained when a mixture of ethyl acetonedicarboxylate and its nitroso-derivative is reduced with zinc dust, melts at  $113\text{--}113.5^\circ$ , is soluble in most organic solvents except light petroleum, and is not easily reduced or brominated.

The corresponding *acid* crystallises with  $H_2O$  in small needles, which turn red in air and melt and decompose at  $220^\circ$ , yielding 2:4-dimethylpyrrole. R. H. P.

Studies in the Pyrrole Group. IV. Condensation of Esters of Amino- $\beta$ -ketonic Acids with 1:2-Diketones and 1:2-Ketone-alcohols. By FRANZ FEIST and ERICH STENGER (*Ber.*, 1902, 35, 1558—1561).—Ethyl aminocrotonate condenses with benzoin, forming *ethyl 4:5-diphenyl-2-methylpyrrole-3-carboxylate*, which separates from methyl alcohol in white crystals and melts at  $202^\circ$ . The *acid*, which was only obtained in an impure state, melts at  $132^\circ$  and forms insoluble *silver*, *calcium*, and *barium* salts.

Analogous condensation with ethyl diketosuccinate yields a mixture of a compound,  $C_{20}H_{30}O_9N_2$ , and ethyl 2-methylpyrrole-3:4:5-tricarboxylate; the former crystallises in small, colourless needles melting at  $149.5^\circ$ , and the latter separates from ether in small, lustrous crystals melting at  $104^\circ$ .

Similar condensations with diacetyl, benzil, and phenanthraquinone gave no definite pyrrole derivatives. R. H. P.

**Condensation of Pyrroles and Ethereal Pyrrolecarboxylates with Aromatic Aldehydes.** By FRANZ FEIST (*Ber.*, 1902, 35, 1647—1655. Compare preceding abstract).—The condensation between pyrrole derivatives and the aldehydes obeys the following rules: (1) only those derivatives condense which contain at least one hydrogen atom combined with a carbon atom of the nucleus; this atom may be either in the  $\alpha$ - or the  $\beta$ -position; (2) when both  $\alpha$ - and  $\beta$ -positions are occupied by substituents, no combination occurs even when an imino-hydrogen atom is present; (3) pyrrole derivatives containing more than one hydrogen atom in the ring may combine with aldehydes in molecular proportions.

These empirical laws indicate that the aldehyde residue at once combines with the carbon atom of the nucleus without forming an intermediate N-derivative. The reaction seems to depend on the reactivity of the double linkings of the pyrrole ring.

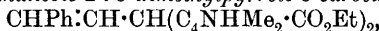
The condensations were produced by melting together the pyrrole derivative and the aldehyde and adding some powdered potassium hydrogen sulphate.

[With B. WIDMER and J. SAKOWITSCH.]—Ethyl phenylmethanebis-2:5-dimethylpyrrole-3-carboxylate,  $CHPh(C_4NHMe_2 \cdot CO_2Et)_2$ , prepared from benzaldehyde and 2:6-dimethylpyrrolecarboxylate, crystallises from dilute alcohol in lustrous leaflets melting at  $228^\circ$ ; it is insoluble in water and not hydrolysed by mineral acids.

Ethyl p-nitrophenylmethanebis-2:5-dimethylpyrrole-3-carboxylate,  $NO_2 \cdot C_6H_4 \cdot CH(C_4NHMe_2 \cdot CO_2Et)_2$ , crystallises from alcohol in yellowish-green needles and melts at  $275.5^\circ$ ; the isomeride from m-nitrobenzaldehyde melts at  $214^\circ$ .

Diethyl p-hydroxy-m-methoxyphenylmethanebis-2:5-dimethylpyrrole-3-carboxylate,  $OMe \cdot C_6H_4(OH) \cdot CH(C_4NHMe_2 \cdot CO_2Et)_2$ , is a crystalline powder obtained by condensation with vanilaldehyde; it melts at  $216^\circ$ .

Ethyl styrylmethanebis-2:5-dimethylpyrrole-3-carboxylate,



from the pyrrole ester and cinnamaldehyde, forms white crystals melting at  $243^\circ$ .

Ethyl o-hydroxyphenylmethanebis-2:5-dimethylpyrrole-3-carboxylate,  $OH \cdot C_6H_4 \cdot CH(C_4NHMe_2 \cdot CO_2Et)_2$ , obtained from salicylaldehyde, is a white powder melting at  $212^\circ$ ; it develops a deep red coloration either with ferric chloride or atmospheric oxygen.

Ethyl methylenedioxyphenylmethanebis-2:5-dimethylpyrrole-3-carboxylate,  $CH_2O_2 \cdot C_6H_3 \cdot CH(C_4NHMe_2 \cdot CO_2Et)_2$ , melts at  $116^\circ$ .

Ethyl phenylmethanebis-2:4-dimethylpyrrole-3-carboxylate, prepared from ethyl 2:4-dimethylpyrrole-3-carboxylate and benzaldehyde, melts at  $188^\circ$ ; the nitro-compound from p-nitrobenzaldehyde crystallises in

yellow needles and melts at  $192^{\circ}$ ; anisaldehyde gives a *product* crystallising in white needles and melting at  $171-172^{\circ}$ .

Ethyl 1-phenyl-2:5-dimethylpyrrole-3-carboxylate and benzaldehyde yield a crystalline condensation *product* melting at  $160^{\circ}$ ; its *p*-nitro-derivative separates in pale yellow needles.

1-Phenylbenzylidenepyrrole, formed by the condensation of 1-pyrrole and benzaldehyde, readily dissolves in acetone and separates from a mixture of this solvent with alcohol as a white powder melting at  $265.5^{\circ}$ ; it has not been ascertained whether this compound has the simple formula  $\text{CHPh}\cdot\text{C}_4\text{NH}_3\text{Ph}$ , or whether it results from a condensation of 2 mols. of the aldehyde with 2 mols. of the base. Another product is formed in the condensation and is separated from the preceding substance by extraction with petroleum; it separates from this solvent as a pale pink powder melting at  $231^{\circ}$  and giving analytical figures corresponding with those required for the formula  $(\text{C}_{18}\text{H}_{15}\text{N})_n$ .  
G. T. M.

**Hydrazides of 2-Pyrrolecarboxylic Acid and of 2-Indolecarboxylic Acid and their Transformations.** By ANTONIO PICCININI and L. SALMONI (*Gazzetta*, 1902, 32, i, 246—253).—The authors have been unable to prepare the 2-amino-derivatives of pyrrole and indole from the 2-carboxylic acids of these bases, but they have obtained the corresponding hydrazides, azoimides, and urethanes.

*Pyrrolylhydrazide*,  $\begin{array}{c} \text{CH}\cdot\text{CH} \\ || \quad | \\ \text{CH}\cdot\text{NH} \end{array} > \text{C}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , prepared by the interaction of hydrazine and methyl pyrrole-2-carboxylate, crystallises from dilute alcohol in compact, colourless prisms which become faintly yellow at  $210^{\circ}$  and melt at  $231-232^{\circ}$ ; it is slightly soluble in methyl or ethyl alcohol or light petroleum and to a greater extent in water. Its aqueous solution energetically reduces Fehling's solution and ammoniacal silver nitrate.

*Benzaldehydepyrrolylhydrazone*,  $\text{C}_4\text{H}_4\text{N}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh}$ , prepared from pyrrolylhydrazide and benzaldehyde, separates from dilute alcohol in shining leaflets melting at  $164-165^{\circ}$ .

*Pyrroylazoimide*,  $\text{C}_4\text{NH}_4\cdot\text{CO}\cdot\text{N} < \begin{array}{c} \text{N} \\ || \\ \text{N} \end{array}$ , obtained by the action of nitrous acid on pyrrolylhydrazide, is deposited in nacreous crystals which melt and evolve gas at  $105^{\circ}$  and are soluble in alcohol or ether. On reduction with zinc and acetic acid, it is converted into carbopyrrolamide.

1-Pyrrolylurethane,  $\text{C}_4\text{NH}_4\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , prepared by boiling pyrrolylhydrazide with absolute alcohol, nitrogen being at the same time evolved, crystallises from light petroleum in long, colourless needles melting at  $55-56^{\circ}$  and rapidly changing in the air to a red mass. The action of nitrous acid on its hydrochloric acid solution yields a *nitroso*-derivative which separates from water or alcohol as a micro-crystalline powder decomposing without melting at  $200-210^{\circ}$ . When heated with acetic anhydride, pyrrolylurethane yields a crystalline *acetyl* derivative. No definite products are formed when the base is boiled with ammonia, alkalis, or hydrochloric acid.

*Indole-1-carboxylic acid hydrazide*,  $C_9H_9ON_2$ , separates from alcohol in shining, nacreous leaflets which soften at  $230^\circ$  and melt at  $241^\circ$ ; it is slightly soluble in water or hydrochloric or acetic acid and its aqueous solution readily reduces silver nitrate.

*Indole-1-carboxylic acid azoimide*,  $C_9H_6ON_4$ , separates in colourless leaflets which are slightly soluble in water and decompose violently at about  $140^\circ$ .

*1-Indole-urethane*,  $C_{11}H_{12}O_2N_2$ , crystallises from light petroleum in compact, colourless prisms melting at  $110^\circ$ , and shows reactions similar to those of the pyrrole compound.

T. H. P.

**Some Compounds of Pyridine.** By J. ARTHUR HAYES (*J. Amer. Chem. Soc.*, 1902, 24, 360—362).—When a solution of antimony tribromide in hydrobromic acid is added to a solution of pyridine hydrobromide, the compound,  $C_5NH_5SbBr_3 \cdot 3HBr$ , is obtained as a yellow, crystalline precipitate, which is soluble in dilute hydrochloric acid and slightly so in alcohol or chloroform.

The compound,  $C_5NH_5SnCl_3 \cdot 3HCl$ , obtained in a similar manner, crystallises in small, white needles, and is soluble in dilute hydrochloric acid, and slightly so in alcohol.

The compound,  $C_5NH_5MnCl_2 \cdot HCl$ , crystallises in salmon-coloured plates and is soluble in alcohol or hydrochloric acid, and slightly so in ether.

E. G.

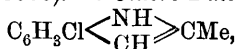
**Some Derivatives of  $\alpha$ -Picoline.** By KARL FEIST (*Arch. Pharm.*, 1902, 240, 178—201. Compare Hardy and Calmels, *Abstr.*, 1887, 1057, and Knudsen, *Abstr.*, 1895, i, 564).— $\gamma$ -Trichloro- $\alpha$ -hydroxypropylpyridine (Einhorn, *Abstr.*, 1892, 75) was prepared, and its *aurichloride*, melting at  $152^\circ$ , *platinichloride*, with  $1\frac{1}{2}H_2O$ , *picrate*, melting at  $167^\circ$ , and the compound,  $C_5H_8ONCl_3 \cdot 5HgCl_2$ , melting at  $148^\circ$  were analysed. The hydrochloride of pyridylacrylic acid is converted into the acid itself, when it is recrystallised from absolute alcohol. The acid is merely converted into the *hydriodide*, which melts at  $196$ — $197^\circ$ , by aqueous hydriodic acid at the ordinary temperature; when it is boiled with hydriodic acid in acetic acid solution, it is reduced to 2-pyridyl- $\beta$ -propionic acid. This melts at  $141^\circ$ ; its *aurichloride*, melting at  $164^\circ$ , and *platinichloride*, with  $2H_2O$ , melting at  $177^\circ$ , were analysed. 2-Pyridyl- $\beta$ -bromopropionic acid forms an *auribromide*, melting at  $151$ — $160^\circ$ , and readily loses hydrogen bromide with regeneration of pyridylacrylic acid; silver acetate precipitates the bromine and forms pyridyl- $\beta$ -lactic acid, which is also formed by the action of silver chloride. The bromo-acid reacts with 33 per cent. alcoholic trimethylamine, best at  $0$ — $8^\circ$ , forming, in addition to pyridylacrylic acid,  *$\beta$ -pyridyltruxillic acid*,  $C_5NH_4 \cdot CH \begin{smallmatrix} \text{CH}(C_5NH_4) \\ \text{CH}(CO_2H) \end{smallmatrix} \cdot CH \cdot CO_2H$ ; the hydrochloride of this melts at  $209^\circ$ , the *aurichloride*, with  $HAuCl_4$ , at  $182^\circ$ , and the *platinichloride*, with  $H_2PtCl_6$ , at  $185$ — $186^\circ$ . The proportion converted into pyridylacrylic acid is increased when the trimethylamine is allowed to react at a higher temperature, or in aqueous instead of alcoholic solution.

2-Pyridyl- $\alpha$ -lactic acid (Einhorn, *loc. cit.*) can be converted into

2-pyridyl- $\alpha$ -bromopropionic acid by heating it with phosphorus tri-bromide at 130—140° in an atmosphere of carbon dioxide in a sealed tube; the auribromide of this acid melts at 195°. By alcoholic trimethylamine, the acid is converted almost entirely into an acid, which, from the analysis and melting point, 182°, of its aurichloride, seems to be identical with  $\beta$ -truxillic acid, but may possibly be  $\alpha$ -truxillic acid,  $C_5NH_4 \cdot CH \begin{smallmatrix} \text{CH}(\text{CO}_2\text{H}) \\ \text{CH}(\text{CO}_2\text{H}) \end{smallmatrix} > CH \cdot C_5NH_4$ . C. F. B.

**Transformation of Meconic Acid Derivatives into Hydroxy-pyridines.** By ALBERTO PERATONER (*Atti Real. Accad. Lincei*, 1902, [v], 11, i, 327—333).—A résumé of the subject. T. H. P.

[Indole Derivatives.] FARBENFABRIKEN VORM. F. BAYER & Co (D.R.-P. 127245 and 128660).—5-Chloro-2-methylindole,



(compare E. Fischer, *Abstr.*, 1886, 805), prepared by heating the *p*-chlorophenylhydrazine of acetone with zinc chloride, and separated by distillation in steam, crystallises in plates and melts at 119°.

2-Phenyl-5-methylindole,  $C_8H_5NMePh$ , and 5-chloro-2-phenylindole,  $C_8H_5NPhCl$ , are pale yellow, crystalline powders melting at 213° and 96°.

1:2:5-Trimethylindole,  $C_8H_4NMe_3$  (E. Fischer, *loc. cit.*), produced from *as-p*-tolylmethylhydrazine and acetone, is readily distilled in steam; it crystallises in colourless leaflets and melts at 56—57°.

2-Phenyl-1:5-dimethylindole,  $C_8H_4NMe_2Ph$ , obtained from *as-p*-tolyl methylhydrazine and acetophenone, crystallises from dilute alcohol in colourless leaflets and melts at 124°.

5-Chloro-1:2-dimethylindole,  $C_8H_4NMe_2Cl$ , produced from *as-p*-chlorophenylmethylhydrazine and acetone, forms leaflets melting at 67°.

5-Chloro-2-phenyl-1-methylindole,  $C_8H_4NMePhCl$ , separates from alcohol in yellow crystals melting at 109°.

2-Phenyl-1-ethylindole forms colourless crystals melting at 86°.

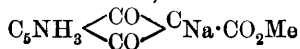
2:5-Dimethyl-1-ethylindole,  $C_8H_4NMe_2Et$ , and 2-phenyl-5-methyl-1-ethylindole,  $C_8H_4NMeEtPh$ , form colourless crystals melting respectively at 47° and 72°.

5-Chloro-2-methyl-1-ethylindole,  $C_8H_4NMeEtCl$ , prepared from *p*-chloro-*as*-ethylphenylhydrazine and acetone, crystallises from light petroleum in rhombic plates and melts at 74°. 5-Chloro-2-phenyl-1-ethylindole,  $C_8H_4NPhCl$ , is an amorphous, yellow powder melting at 107°.

The preceding indole derivatives all give the colour reaction with the pine-wood shaving, and combine with auramine or diaminobenzophenone or its derivatives, yielding basic colouring matters.

G. T. M.

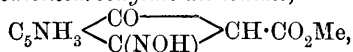
**Synthesis of Pyrindene Derivatives.** By KARL BITTNER (*Ber.*, 1902, 35, 1411—1413).—By condensing dimethyl quinolinate with methyl acetate by means of sodium, the sodium salt,



or  $C_5NH_3 \begin{smallmatrix} \diagup C(ONa) \\ \diagdown CO \end{smallmatrix} \rangle C \cdot CO_2Me$ , of *methyl pyrindanedione carboxylate*, is obtained in the form of yellow needles which rapidly resinify in the air; on acidifying a solution of the *sodium* derivative, yellow crystals of the parent substance,  $C_{10}H_7O_4N$ , separate; the *barium* salt,  $(C_{10}H_6O_7N)_2Ba$ , forms yellow needles.

*Anhydrobispyrindanedione*,  $C_5NH_3 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} \rangle C:C \begin{smallmatrix} \diagup CH_2 \\ \diagdown C_5NH_3 \end{smallmatrix} \rangle CO$ , obtained by heating a concentrated aqueous solution of the foregoing sodium derivative with glacial acetic acid for several hours at  $100^\circ$ , is insoluble in the ordinary solvents.

*Methyl pyrindanedione carboxylate monoxime*,



obtained from the sodium derivative and hydroxylamine, crystallises from water in yellow needles; a dioxime could not be obtained.

W. A. D.

**Nitroquinolones and Nitrocarbostyrils.** By HERMAN DECKER (*J. pr. Chem.*, 1902, [ii], 65, 300—303. See Abstr., 1902, i, 654).—*Trinitro-1-methyl-2-quinolone*, obtained when 5-nitro-1-methyl-2-quinolone is treated with fuming nitric acid, separates from toluene either in lustrous, pointed needles with toluene of crystallisation, or in short, yellow, compact prisms; it melts and decomposes at  $221^\circ$ . The analogous *trinitro-1-ethyl-2-quinolone* crystallises with toluene and melts and decomposes at  $222^\circ$ .

6-Nitro-1-ethyl-2-quinolone, when treated with nitric acid in the cold, forms a *nitrate* which crystallises in bright yellow needles and melts at  $183^\circ$ .

*Dinitro-1-ethyl-2-quinolone*, obtained along with the trinitro-compound when 5-nitro-1-ethyl-2-quinolone is nitrated with warm fuming nitric acid, crystallises from alcohol in large, pointed needles, turns brown at  $175$ — $180^\circ$ , sinters at  $192^\circ$ , and melts and decomposes at  $197^\circ$ .

R. H. P.

**Bromo-derivatives of Quinophthalone.** By ALEXANDER EIBNER and H. MERKEL (*Ber.*, 1902, 35, 1656—1662. Compare Abstr., 1901, i, 611).—The compound obtained by mixing a chloroform or glacial acetic acid solution of quinophthalone and bromine is not a tribromoquinophthalone, but contains four atoms of bromine; it is, however, very unstable, losing bromine at the ordinary temperature and parting with the whole of the halogen on gentle warming; all the solvents affect it except chloroform, from which it separates in orange-yellow crystals. The following reactions indicate that it is a perbromide,

and that the formula  $\begin{smallmatrix} C_6H_4 \\ \diagdown CO \cdot O \end{smallmatrix} \rangle C:CBr \cdot C_9NH_5Br \begin{smallmatrix} \diagup Br \\ \diagdown Br \end{smallmatrix}$  best expresses its

behaviour. The substance, when treated with water or alcohol, yields bromoquinophthalone; ammonia or sulphurous acid, on warming, removes the halogen regenerating quinophthalone; iodine is liberated from an acid solution of potassium iodide. Treatment with cold ammonia indicates that two bromine atoms are in the "perbromide"



condition, for 2 mols. of this reagent are decomposed with the evolution of nitrogen by 3 mols. of the bromo-derivative.

Bromoquinophthalone is most readily obtained by the action of alcohol or ammonia on the tetrabromide at the ordinary temperature, and crystallises from chloroform in pale yellow, hexagonal plates melting at  $179^{\circ}$ ; its hydrobromide is an unstable, red salt which is formed, together with the preceding perbromide, by the action of bromine on quinophthalone, and decomposes at  $100^{\circ}$  into quinophthalone and bromine. The *perbromide* of bromoquinophthalone,  $C_{18}H_{11}O_2NBr_6$ , results from the action of bromine in chloroform solution; it is very unstable, losing bromine at the ordinary temperature, and is decomposed by alcohol, water, or ammonia. These reactions indicate that the preceding bromoquinophthalone has the formula  $\begin{matrix} C_6H_4 \\ CO_2 \end{matrix} > C:CBBr \cdot C_9NH_6$ .

*p*-Toluquinophthalone also yields an orange-yellow, crystalline *tetrabromide*,  $C_{19}H_{13}O_2NBr_4$ .  
G. T. M.

**Dinitrocarbazole.** ERNST WIRTH (D.R.-P. 128853).—A *dinitrocarbazole* is readily prepared by agitating a 10 per cent. benzene solution of nitrosocarbazole (obtained by treating crude carbazole with nitrous acid) with nitric acid of sp. gr. 1.36 until a green coloration is no longer developed with concentrated sulphuric acid. The product is sparingly soluble in the ordinary solvents, but dissolves in hot nitrobenzene or aniline, and separates on cooling as a yellow powder not melting below  $320^{\circ}$ . On reduction, it yields diaminocarbazole.

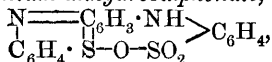
G. T. M.

**9-Iodoacridine.** KALLE & Co. (D.R.-P. 126795. Compare Abstr., 1901, i, 166).—9-Iodoacridine, prepared by heating together alcoholic solutions of 9-bromoacridine and sodium iodide, separates in a crystalline form and melts at  $171^{\circ}$ ; the yield is practically quantitative.

G. T. M.

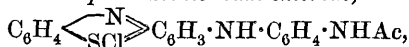
**Thiazine Colouring Matters.** AKTIENGESSELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 126410).—*Phenylthiazine* (3-anilinophenazothionium chloride),  $C_6H_4 \begin{matrix} \text{N} \\ \text{SCI} \end{matrix} > C_6H_5 \cdot NHPh$ , readily obtained from thiodiphenylamine, aniline (1 mol.), and alcoholic ferric chloride, crystallises from dilute hydrochloric acid in coppery leaflets which dissolve in water or alcohol to a bluish-green solution; the free thio-base is precipitated by ammonia or the alkali hydroxides in pink flocks.

3-Anilinophenazothionium anhydrosulphonate,

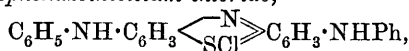


produced from thiodiphenylamine, sulphanilic acid, and ferric chloride, is a dark green, crystalline powder.

3-*p*-Acetylanilinoaminophenazothionium chloride,



obtained in a similar manner from monoacetyl-*p*-phenylenediamine, separates in coppery needles. The preceding compounds dye tannin-mordanted cotton a dark green.

*3 : 9-Dianilinophenazothionium chloride,*

prepared by the action of ferric chloride on 1 mol. of thiodiphenylamine and 2 mols. of aniline, crystallises from hot alcohol in needles having a brass-like lustre which are sparingly soluble in cold water, but dissolve more readily in the boiling solvent or in alcohol. The *monoacetyl* derivative,  $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{N}\\\text{S}\text{Cl}\end{smallmatrix}\right\rangle\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , obtained by heating an alcoholic solution of 4-*p*-acetylanilinoaminophenazothionium chloride with aniline hydrochloride, is precipitated from its blue aqueous solution on adding sodium chloride; it dissolves in alcohol to a bluish-green solution. G. T. M.

**Phenazothionium Salts.** AKTIENGESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 126602).—*Phenazothionium bromide*,

$\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{N}\\\text{SBr}\end{smallmatrix}\right\rangle\text{C}_6\text{H}_4$ , prepared by mixing together at  $-15^\circ$  to  $-20^\circ$  alcoholic solutions of thiodiphenylamine and bromine in the presence of a small amount of hydrobromic acid, separates as a brownish-green, crystalline powder with a metallic lustre. The oxidation may also be effected in benzene, chloroform, carbon disulphide, or ethereal solution, and under these conditions the bromide is completely precipitated, being insoluble in these solvents; it undergoes decomposition when dissolved in water or alcohol, but is rendered more stable by the presence of acid. The solution, when boiled, yields a mixture of thiodiphenylamine, and the substance  $\text{O}\cdot\text{C}\left(\begin{smallmatrix}\text{CH}\cdot\text{CH}\cdot\text{C}\cdot\text{N}\\\text{CH}\cdot\text{C}\cdot\text{S}\end{smallmatrix}\right)\text{C}_6\text{H}_4$ .

The *double salt* of phenazothionium chloride and ferrous chloride,  $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{N}\\\text{S}\text{Cl}\end{smallmatrix}\right\rangle\text{C}_6\text{H}_4\cdot\text{FeCl}_2$ , produced by oxidising thiodiphenylamine with an alcoholic solution of ferric chloride acidified with hydrochloric acid, separates as a dark greenish-brown powder.

*Phenazothionium picrate*, formed when the preceding experiments are carried out in the presence of picric acid, separates out as a yellowish-green powder.

These phenazothionium derivatives yield thiazine colouring matters on condensation with amines. G. T. M.

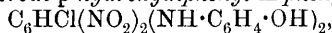
**Pyrazoles from 1 : 3-Diketones and Alkyl Diazoacetates.** By AUGUST KLAGES (*J. pr. Chem.*, 1902, [ii], 65, 387—393. Compare this vol., i, 236).—Acetylacetone and ethyl diazoacetate condense in a warm, very dilute solution of sodium hydroxide to *ethyl 5-acetyl-4-methylpyrazole-3-carboxylate*,  $\text{CAc}\left\langle\begin{smallmatrix}\text{NH}\cdot\text{N}\\\text{CMe}\end{smallmatrix}\right\rangle\text{C}\cdot\text{CO}_2\text{Et}$ , which crystallises from water in long, colourless needles, melts at  $123-124^\circ$ , boils at  $202^\circ$  under 26 mm. pressure, and is easily soluble in alcohol, chloroform, glacial acetic acid, or ammonia. With concentrated aqueous sodium hydroxide, it forms a *sodium* derivative, and with silver nitrate a white, flocculent precipitate,  $\text{C}_9\text{H}_{11}\text{O}_3\text{N}_2\text{Ag}$ . A mol. weight deter-

mination gave 194;  $C_9H_{12}O_3N_2$  requires 196. The *oxime* forms glistening, colourless leaflets which melt at  $165^\circ$ . On hydrolysis of the ester, the *acid* is obtained in colourless needles which contain  $H_2O$  and melt at  $233^\circ$ .

Acetyl-4-methylpyrazolecarboxylic acid is oxidised by potassium permanganate in alkaline solution to 4-methylpyrazoledicarboxylic acid,  $C_3N_2HMe(CO_2H)_2$ , which melts at  $293^\circ$ . Distillation of the silver salt in a stream of carbon dioxide yields an oil having the properties of 4-methylpyrazole (Abstr., 1901, i, 167). Ethyl diazoacetate and propionyl acetone yield a pyrazole derivative,  $C_{10}H_{14}O_3N_2$ , which melts at  $59^\circ$ , and forms an *oxime* and a *semicarbazone*. On hydrolysis, it yields a *ketopyrazolecarboxylic acid* which melts at  $191^\circ$ . G. Y.

**Compounds of 1-Phenyl-2:3-dimethyl-5-pyrazolone and its Derivatives with the Methyl Aminohydroxybenzoates.** ALFRED EINHORN (D.R.-P. 126340. Compare Patein and Dufau, Abstr., 1896, i, 188, 650; 1897, i, 375, 543).—*Compounds* having the nature of salts are obtained by melting together 1-phenyl-2:3-dimethyl-5-pyrazolone or one of its homologues and methyl 1:2:4- or 1:2:5-aminohydroxybenzoate. Methyl 1:2:4-aminohydroxybenzoate yields with 1-phenyl-2:3-dimethyl-5-pyrazolone and 1-phenyl-2:3-dimethyl-4-dimethylamino-5-pyrazolone crystalline compounds melting at  $82^\circ$  and  $72^\circ$  respectively. The corresponding ester of the 1:2:5-acid, when combined with these pyrazolone derivatives, gives rise to similar substances melting at  $93^\circ$  and  $86^\circ$  respectively. G. T. M.

[2:6-Dinitro-4-chloro-*pp*-dihydroxydiphenyl-*m*-phenylene Diamine.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 127441).—2:6-Dinitro-4-chlorodi-*p*-hydroxydiphenyl-*m*-phenylenediamine,



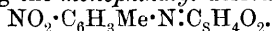
prepared by heating together 1:2:4-trichloro-3:5-dinitrobenzene, *p*-aminophenol hydrochloride and crystallised sodium acetate in alcoholic solution first at  $40^\circ$  and finally at the boiling point, separates from alcohol as an orange-coloured, crystalline powder which sinters at  $155^\circ$  and decomposes at  $215^\circ$ . It is soluble in alcohol and in sodium hydroxide solution. G. T. M.

[Phthalyltolylenediamines.] J. R. GEIGY & Co. (D.R.-P. 126964. Compare Biedermann, Abstr., 1877, ii, 783).—The 4-monophthalyl derivative (m. p.  $192^\circ$ ) obtained by heating equivalent proportions of phthalic anhydride and 2:4-tolylenediamine probably has the

constitution indicated by the formula

$$\begin{array}{c} \text{CH}=\text{CH}-\text{C} \cdot \text{N} \cdot \text{C}-\text{O} \\ \text{CMe} \cdot \text{C}(\text{NH}_2) \cdot \text{CH} \quad \text{C}_6\text{H}_4 \cdot \text{CO} \end{array}$$

it is also prepared by condensing *o*-nitro-*p*-toluidine with phthalic anhydride and reducing the *monophthalyl* derivative,



This nitro-compound crystallises from glacial acetic acid in silky needles, and melts at  $222^\circ$ ; its isomeride derived from *p*-nitro-*o*-toluidine melts at  $232^\circ$  and yields the isomeric 2-monophthalyl-2:4-tolylenediamine, a colourless substance melting at  $168^\circ$ .

Both these monophthalyl derivatives, on further treatment with phthalic anhydride, yield the dipthalyl compound melting at 232°.

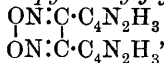
G. T. M.

**Electrolytic Reduction of Oximes and Phenylhydrazones in Sulphuric Acid.** By JULIUS TAFEL and EPHRAIM PFEFFERMANN (*Ber.*, 1902, 35, 1510—1518. Compare Abstr., 1894, i, 579).—Ethylidene-phenylhydrazine, when reduced at 0—4° in 50 per cent. sulphuric acid by a current of 120 amperes, gives rise to a mixture of ethylamine and aniline. Acetophenylhydrazone, under these conditions, yields aniline and isopropylamine. Benzylidenephylhydrazone, when dissolved in a mixture of dilute sulphuric and acetic acids, furnishes, on electrolysis, benzylamine, benzylaniline, and aniline.

The electrolysis of acetoxime and benzaldoxime leads to the production of isopropylamine and benzylamine respectively, the yields of these derivatives being about two-thirds of the theoretical. Acetophenoneoxime and benzophenoneoxime yield  $\alpha$ -phenylethylamine and benzhydrylamine respectively. Camphoroxime gives rise to bornylamine. Glyoxime, on electrolysis, is decomposed into ammonia and glyoxal; methylglyoxime, under similar conditions, does not yield any diamine, the only base isolated from the product being ammonia.

G. T. M.

**The Methylated Pyrimidines.** By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1902, 35, 1569—1575).—I. Derivatives of 4-methylpyrimidine.—2:6-Dichloro-4-methylpyrimidine is converted by chlorine into a mixture of the tetra- and penta-chloro-derivatives. *Pentachloromethylpyrimidine*,  $C_5H_2N_2Cl_5$ , crystallises in vitreous prisms or octahedra melting at 82—83°. *Tetrachloroaminomethylpyrimidine*,  $C_5H_2N_2Cl_4 \cdot NH_2$ , is prepared by the action of alcoholic ammonia on the foregoing compound, and crystallises in short prisms, melting and decomposing at 225—227° after sintering at 220°. *5-Bromo-2:6-diamino-4-methylpyrimidine*,  $C_4N_2Me(NH_2)_2Br$ , is formed by the action of bromine water on 2:6-diamino-4-methylpyrimidine hydrobromide, and crystallises in oblique prisms or rhombohedra, which sinter at 185° and melt and decompose at 188—189°. The substance formed by the action of fuming nitric acid on 4-methylpyrimidine (Abstr., 1900, i, 53) is probably 4:4-dipyrimidylglyoxime peroxide,



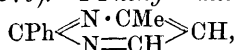
and by reduction with hydriodic acid and phosphonium iodide is converted into the corresponding base, 4:4-dipyrimidylethylenediamine,  $C_4N_2H_5 \cdot CH(NH_2) \cdot CH(NH_2) \cdot C_4N_2H_3$ , which crystallises in colourless plates, sinters at 132°, and melts and decomposes at 142—145°. The *hydriodide*,  $C_{10}H_{12}N_6 \cdot 4HI$ , forms lemon-yellow, pointed plates, and the *hydrochloride*,  $C_{10}H_{12}N_6 \cdot 4HCl$ , forms colourless needles. The *diacetyl* derivative,  $C_{10}H_{10}N_6Ac_2$ , crystallises in flat needles and melts at 255°.

II. Derivatives of 2:4-dimethylpyrimidine.—This compound is converted by nitric acid into *dimethylpyrimidylglyoxime peroxide*,  $ON:C \cdot C_4N_2H_2Me$   
 $ON:C \cdot C_4N_2H_2Me'$ , which crystallises in rhombic tablets, sinters at

132°, and melts at 134—135°. The *platinichloride* is a yellow, crystalline powder, which does not melt below 270°. The corresponding base, *dimethylpyrimidylethylenediamine*, crystallises in needles, sinters at 158°, and melts and decomposes at 161°; the *hydriodide* crystallises in rhombic plates. The base is accompanied by a substance of lower melting point, the nature of which has not yet been ascertained.

A. H.

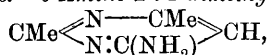
**The Methylated Pyrimidines.** By K. F. M. JULIUS SCHMIDT (*Ber.*, 1902, 35, 1575—1579).—2-Phenyl-4-methylpyrimidine,



is prepared by the reduction of 4:6-chloro-2-phenyl-4-methylpyrimidine, and is a refractive liquid which boils at 279° and solidifies in small prisms melting at 22.5°. The *platinichloride* forms yellow spheroids, the *nitrate* melts at 113°, and the *picrate* crystallises from alcohol. 6-Chloro-2:4-dimethylpyrimidine,  $\text{CMe} \begin{array}{c} \text{N} \cdot \text{CMe} \\ \diagdown \quad \diagup \\ \text{N} = \text{CCl} \end{array} \text{CH}$ , is

prepared by the action of phosphorus oxychloride on hydroxydimethylpyrimidine, and is an oil which boils at 182° and solidifies at 7°.

On reduction, it yields 2:4-dimethylpyrimidine,  $\text{CMe} \begin{array}{c} \text{N} \cdot \text{CMe} \\ \diagdown \quad \diagup \\ \text{N} = \text{CH} \end{array} \text{CH}$ , which boils at 146° and has the sp. gr. 1.168 at 13.8°/16°. The base has an odour like that of acetamide and yields crystalline double salts with the usual reagents. 6-Amino-2:4-dimethylpyrimidine,



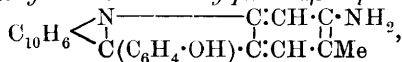
is obtained by the action of alcoholic ammonia on 6-chloro-2:4-dimethylpyrimidine and crystallises in fan-shaped aggregates of needles melting at 183°. The *platinichloride* forms yellow needles, the *picrate* melts at 214°, and the *mercurichloride* forms slender needles. 6-Amino-2:4-dimethylpyrimidine melts at 104° and is a mono-acid base.

6-Thiol-2:4-dimethylpyrimidine,  $\text{C}_4\text{N}_2\text{HMe}_2\text{SH}$ , is prepared by the action of alcoholic potassium hydrosulphide on the chloro-compound and forms yellow crystals which become brown at 225° and melt at 230°. The corresponding *disulphide*,  $\text{S}_2(\text{C}_4\text{N}_2\text{HMe}_2)_2$ , crystallises in short needles melting at 99°. As a rule, the disulphides in the pyrimidine series melt at lower temperatures than the mercaptans.

A. H.

**Naphthacridine Colouring Matters.** FRITZ ULLMANN (D.R.-P. 127586. Compare this vol., i, 55, 56, 183).—2-Amino-5-phenyl-3-methylpheno- $\alpha\beta$ -naphthacridine,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \\ \diagdown \quad \diagup \\ \text{CPh} \cdot \text{C} : \text{CH} \cdot \text{C} : \text{CH} \cdot \text{C} : \text{NH}_2 \\ | \\ \text{C} : \text{CH} \cdot \text{CMe} \end{array}$ , is prepared either by heating benzylidene-2:4-tolylenediamine with  $\beta$ -naphthol or by fusing a mixture of benzaldehyde,  $\beta$ -naphthol, and the diamine at 180—190°. If the three nitrobenzaldehydes are employed in this condensation, the corresponding nitroacridine bases are produced.

5-p-Hydroxyphenyl-2-amino-3-methylpheno- $\alpha\beta$ -naphthacridine,

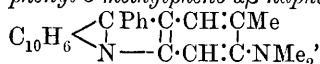


n n 2

is a sparingly soluble, yellow powder formed by the interaction of *m*-tolylenediamine, *p*-hydroxybenzaldehyde, and  $\beta$ -naphthol. Similar acridine derivatives are obtained by employing *p*-chlorobenzaldehyde and  $\beta$ -hydroxy- $\alpha$ -naphthaldehyde, the product from the latter crystallising in yellow needles melting at 220°. G. T. M.

**Naphthacridine Colouring Matters.** FRITZ ULLMANN (D.R.-P. 128754. Compare this vol., i, 240).—Naphthacridine derivatives are obtained by heating together  $\beta$ -naphthol and the benzyldiene derivatives of the monoalkyl or the *as*-dialkyl-*m*-diamines.

*2-Dimethylamino-5-phenyl-3-methylpheno- $\alpha\beta$ -naphthacridine,*



is prepared by condensing together 2-ethyl-*m*-tolylenediamine, benzaldehyde, and  $\beta$ -naphthol at 180—200°.

Similar bases are produced from 2-methyl-*m*-tolylenediamine, *as*-dimethyl-*m*-tolylenediamine, and the corresponding derivatives of *m*-phenylenediamine.

*2-Benzyl-m-tolylenediamine*, which also yields an acridine derivative, is prepared from benzyl-4-nitro-*o*-toluidine (m. p. 124°); it crystallises from water in sparingly soluble, white needles and melts at 62°.

The properties of the acridine bases are tabulated. G. T. M.

**2:3:5:6-Tetraphenyl-*s*-piperazine.** JULIUS SCHMIDT (D.R.-P. 126798).—*s*- $\alpha$ -Dinitrodiphenylethylene,  $\text{NO}_2 \cdot \text{C} \cdot \text{Ph}$ , and its  $\beta$ -isomeride,

$\text{NO}_2 \cdot \text{C} \cdot \text{Ph}$   
 $\text{NO}_2 \cdot \text{C} \cdot \text{Ph}$ , produced by passing nitrous fumes into an ethereal solution of toluene, melt respectively at 186—187° and 105—107° (compare Sudborough, Trans., 1897, 71, 223); the  $\alpha$ -compound is much less soluble than its isomeride in the ordinary solvents. *s*-Dinitrodiphenylethane, produced by passing nitrogen tetroxide into a benzene solution of stilbene, crystallises in white, silky needles and melts at 235—236°; it may also be prepared by passing nitrous fumes into an ethereal solution of stilbene and decomposing the stilbene nitrosite (m. p. 195—197°) thus obtained by boiling with glacial acetic acid.

2:3:5:6-Tetraphenylpiperazine,  $\text{CHPh} \cdot \text{NH} \cdot \text{CHPh}$   
 $\text{CHPh} \cdot \text{NH} \cdot \text{CHPh}$ , is obtained as hydrochloride by reducing the preceding compound or either of the *s*-dinitrodiphenylethylenes with zinc dust and glacial acetic acid, rendering the mixture alkaline, extracting with ether, distilling off the solvent, evaporating down the hydrochloric acid solution of the residue, and finally recrystallising the product from the concentrated acid. The hydrochloride crystallises in white needles melting at 254—256°, the platinichloride forms golden-yellow leaflets melting at 204°. The base is a dark yellow oil which partially solidifies; it probably consists of a mixture of isomerides.

The mother liquors from the hydrochloride just described contains the hydrochloride of a stereoisomeric base which melts at 230°.

G. T. M.

**Conversion of 1-Arylaminoanthraquinones into Acridine Derivatives.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 126444).—Acridine derivatives are produced from the 1-arylaminoanthraquinones by condensing these substances in the presence of dehydrating agents.

The *base*,  $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \text{---} \text{C}_6\text{H}_3\text{Me} \\ | \quad | \quad | \\ \text{CO} \text{---} \text{C}_6\text{H}_3 \text{---} \text{N} \end{array}$ , prepared by heating at 150° a

mixture of 1-*p*-toluidinoanthraquinone and 70 per cent. sulphuric acid, crystallises from dilute alcohol in yellowish-brown needles; its sulphonic acid, obtained from 1-*p*-toluidinoanthraquinonesulphonic acid, is a soluble substance separating in brick-red crystals and dyeing unmordanted wool. The corresponding *base* from 1-anilinoanthraquinone crystallises in golden-yellow leaflets.

The *diamine*,  $\begin{array}{c} \text{N} \text{---} \text{C}_6\text{H}_3 \cdot \text{C} \text{---} \text{C}_6\text{H}_4 \\ | \quad | \quad | \\ \text{C}_6\text{H}_4 \text{---} \text{C} \text{---} \text{C}_6\text{H}_3 \text{---} \text{N} \end{array}$ , prepared from 1:5-dianilinoanthraquinone separates in dark blue crystals; its dimethyl homologues obtained from 1:5- and 1:4-di-*p*-toluidinoanthraquinones form dark blue and dark red crystals respectively. Other complex acridine bases of this type are described in the patent, the properties of the whole group being exhibited in tabular form.

G. T. M.

**Constitution of the Urazoles.** By MAX BUSCH (*Ber.*, 1902, 35, 1562—1565. Compare this vol., i, 321).—1-Phenylurazole is converted by ethyl iodide and alcoholic potash into 1-*phenyl*-2:4-dimethylurazole, which forms large, colourless crystals melting at 93—95°. Both the methyl groups are united with nitrogen, as no methoxyl is found by Zeisel's test. When boiled with dilute aqueous soda, 1-*phenyl*-2:4-dimethylsemicarbazide,  $\text{NHPh} \cdot \text{NMe} \cdot \text{CO} \cdot \text{NHMe}$ , is formed and crystallises in snow-white needles melting at 135—136°; a small amount of 1-phenyl-2-methylurazole is also produced.

The constitution of phenyldimethylurazole renders it probable that phenylurazole has the formula  $\text{NH} \begin{array}{c} \text{CO} \cdot \text{NPh} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{NH} \end{array}$  and does not contain the hydroxyl group as supposed by Acree (this vol., i, 242). A. H.

**Herzig and Meyer's Method of Estimating Methyl.** By MAX BUSCH (*Ber.*, 1902, 35, 1565—1567).—1-Phenyl-4-methylanilino-urazole,  $\text{NPhMe} \cdot \text{N} \begin{array}{c} \text{CO} \cdot \text{NPh} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{NH} \end{array}$ , the constitution of which is known from its method of preparation, does not conform to Herzig and Meyer's rule, but yields a portion of its methyl in the form of methyl iodide when boiled with hydriodic acid. This appears to be due to the presence of the neighbouring carbonyl group, since benzoylphenylmethylhydrazine behaves in the same way. On the other hand, acetyl- and benzoyl-methylaniline do not yield any methyl iodide when treated in this way. The production of methyl iodide in these circumstances cannot, therefore, be taken as a conclusive proof of the presence of methoxyl, although its non-production may be taken as a proof of the absence of this group. A. H.

**Action of Phenylhydrazine on Acylthiocarbamic and Acyl iminothiocarbamic Esters. Pyrro- $\alpha\beta$ '-diazole [1:2:4-Triazole] Derivatives.** By HENRY L. WHEELER and ALLING P. BEARDSLEY (*Amer. Chem. J.*, 1902, **27**, 257—270).—When phenylhydrazine reacts with acylurethanes, condensation occurs between the  $\cdot\text{NH}_2$  group of the hydrazine and the acyl group of the urethane with the formation of 1:3-dialkyl-1:2:4-triazoles [1:3-dialkylpyrrodiazoles]. With acylthiourethanes, on the other hand, the reaction takes place between the  $\cdot\text{NH}_2$  group of phenylhydrazine and the ester group of the thiourethane, giving rise to the isomeric 1:5-dialkyl-1:2:4-triazoles. This difference in behaviour is explained as due to the tendency of the hydrogen of the  $\cdot\text{NH}_2$  group in phenylhydrazine to react rather with sulphur than with oxygen; this tendency to react with the groups here concerned may be expressed graphically, thus:  $>\text{C}\cdot\text{S}\cdot\text{R} > \text{C}\cdot\text{S} > \text{C}\cdot\text{O} > \text{C}\cdot\text{O}\cdot\text{R}$ . The authors have studied the action of phenylhydrazine on the following substances.

Methyl benzoylthiocarbamate, when warmed in alcoholic solution with a mol. proportion of the hydrazine for several hours at  $100^\circ$ , furnishes 3-hydroxy-1:3-diphenyl-1:2:4-triazole identical with that prepared by Young (*Trans.*, 1895, **67**, 1063).

Benzyl benzoyldithiocarbamate reacts with phenylhydrazine in the cold, furnishing 3-mercapto-1:5-diphenyl-1:2:4-triazole, which crystallises from alcohol in fine, colourless needles soluble in hot benzene and melting at  $187\text{--}187.5^\circ$ . When heated with aniline in sealed tubes at  $270\text{--}300^\circ$  for 12 hours, it furnishes the corresponding monosulphide,  $\text{S}(\text{C}_{14}\text{H}_{10}\text{N}_3)_2$ , which forms pinkish-brown needles melting at  $198^\circ$ . The disulphide, formed when the mercaptotriazole is treated with sodium ethoxide and iodine in alcohol, crystallises in colourless pyramids or arrow-head-shaped crystals melting at  $174^\circ$ . The benzoyl derivative forms colourless needles melting at  $138.5^\circ$ . The methyl ether is produced by the action of methyl iodide on the mercaptotriazole, and crystallises from alcohol in colourless tablets or hexagonal plates melting at  $102\text{--}103^\circ$ . The ethyl ether forms colourless prisms melting at  $97^\circ$ . The condensation product with ethyl acetate consists of colourless prisms melting at  $67^\circ$ , and the benzyl ether crystallises from alcohol in spherical clusters of flattened, colourless prisms melting at  $100\text{--}100.5^\circ$ . The constitution of the triazole was ascertained by its synthesis from phenylthiosemicarbazide and benzaldehyde by the action of ferric chloride.

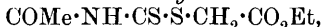
Ethyl benzoyldithiocarbamate reacts in the cold with phenylhydrazine in alcoholic solution, forming mercaptan and benzoylphenylthiosemicarbazide. The latter crystallises from alcohol in colourless, six-sided plates or tablets, or when suddenly cooled in long, slender prisms melting at  $136\text{--}137^\circ$ . When heated alone or with a little phenylhydrazine, or even by solution in alkali and reprecipitation with hydrochloric acid, it is converted into the 3-mercapto-1:5-diphenyl-1:2:4-triazole already described.

Dibenzoylimidothiobenzylethylene ether,  $\text{C}_9\text{H}_4[\text{S}\cdot\text{C}(\text{S}\cdot\text{CH}_2\text{Ph})\cdot\text{N}\cdot\text{COPh}]_2$ , prepared by the action of ethylene bromide on benzoyldithiobenzylcarbamate in presence of sodium ethoxide, crystallises from alcohol in fine needles, colourless, but with a faint green tinge, melting at  $93.5\text{--}94^\circ$ ,



and reacts with phenylhydrazine to form the 3-benzylmercapto-1 : 5-di-phenyltriazole already described.

The *ethyl acetate derivative of acetyldithiocarbamic acid*,



prepared by warming ethyl thiocanoacetate with thioacetic acid, forms yellow needles or slender prisms from benzene or light petroleum and melts at 82°. When heated with phenylhydrazine for several hours at 100°, it forms 3-mercapto-1-phenyl-5-methyl-1 : 2 : 4-triazole, which crystallises from alcohol in colourless prisms melting at 163—164°.

Ethyl benzoyliminomonothiocarbonate,  $\text{COPh} \cdot \text{N} \cdot \text{C}(\text{SEt}) \cdot \text{OEt}$ , reacts with phenylhydrazine in benzene solution at the atmospheric temperature, and after a few hours radiating groups of colourless needles melting at 136° separate of *benzoyl-ψ-ethylphenylsemicarbazide*,



which, when heated in alcoholic solution with phenylhydrazine, is converted into 3-ethoxy-1 : 5-diphenyl-1 : 2 : 4-triazole (Young, *loc. cit.*).

*n*-Propyl benzoyldithiocarbamate reacts with *p*-tolylhydrazine to form 3-mercapto-5-phenyl-1-*p*-tolyl-1 : 2 : 4-triazole, which crystallises from alcohol in needles or prisms melting at 168°.

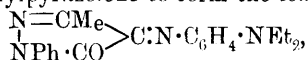
5-Mercapto-1 : 3-diphenyl-1 : 2 : 4-triazole, obtained by the interaction of formylphenylhydrazine with benzoyl thiocyanate, crystallises from alcohol in white, hair-like needles which sinter and melt at about 248—249°. A second substance, insoluble in alkalis, is formed in this reaction, which crystallises from alcohol in slender prisms or needles melting at 119—120°. When heated with dilute alkalis, it dissolves with the formation of aniline or phenylhydrazine and a benzoate, whence the authors conclude that it is probably 1-benzoylimino-2-phenylthiodiazoline,  $\text{N} \begin{smallmatrix} \text{CH} \cdot \text{S} \\ \text{N} \cdot \text{Ph} \end{smallmatrix} > \text{C} \cdot \text{N} \cdot \text{COPh}$ .

*αα*-Carbethoxyphenylsemicarbazide, resulting from the interaction of phenylsemicarbazide with ethyl chlorocarbonate at 100°, crystallises from a mixture of alcohol and benzene in bunches of fine, hair-like needles, melts at 171·5°, and dissolves readily in alcohol, but only sparingly in benzene. With sodium hydroxide, sodium ethoxide, or acetyl chloride it furnishes phenylurazole, and is apparently identical with the supposed dicarbethoxyphenylsemicarbazide described by Acree (Abstr., 1902, i, 242). T. A. H.

*αs-o*-Diaminodibenzylhydrazine. By THEO ULMER (*Ber.*, 1902, 35, 1567—1569).—When dinitrodibenzylnitrosoamine is reduced at 15° by zinc dust in presence of alcoholic acetic acid, it yields *diaminodibenzylhydrazine hydrochloride*, which crystallises in small, colourless plates melting above 260°. The free base,  $\text{NH}_2 \cdot \text{N}(\text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2)_2$ , forms soft, white needles melting indefinitely at 64—65°. It decomposes rapidly on preservation, but has all the properties of a hydrazine and yields with acetic anhydride the triacetyl derivative previously described by Busch and Weiss (Abstr., 1900, i, 699). A. H.

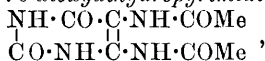
**Ketopyrazolone.** I. By FRANZ SACHS and HERMANN BARSCHALL (*Ber.*, 1902, 35, 1437—1439. Compare Pschorr, *Inaug. Diss. Jena*, 1894; Knorr, Abstr., 1887, 601).—*p*-Nitrosodiethylaniline condenses

with 1-phenyl-3-methylpyrazolone to form the compound



which forms large, dark green glistening crystals and melts at 117°. The corresponding *dimethylamino*-compound separates from alcohol in small, dark green crystals, melts at 187°, and is less soluble than the diethyl compound. Both compounds are hydrolysed by mineral acids to a diamine base and 1-phenyl-3-methylketopyrazolone,  $\text{N} \begin{array}{c} \text{CMe} \cdot \text{CO} \\ \swarrow \searrow \\ \text{NPh} \cdot \text{CO} \end{array}$ , the isatine of the series, which sublimes, or separates from light petroleum, in bronze-coloured, glistening crystals and melts at 119°. The hydrate melts at 71°, the oxime at 157°, and the phenylhydrazone at 155° (Pschorr, *loc. cit.*). The diketone condenses with *o*-phenylenediamine to a cinnabar-red *azine* which melts at 225°. T. M. L.

4:5-Diacetyldiaminouracil. C. F. BOEHRINGER & SÜHNE (D.R.-P. 126797. Compare this vol., i, 125).—4:5-Diacetyldiaminouracil (4:5-diacetyldiamino-2:6-dioxydihydropyrimidine),



produced together with 8-methylxanthine by condensing uric acid with acetic anhydride in the presence of pyridine, quinoline, or dimethylaniline, crystallises from water in felted aggregates of slender needles, sinters at 300°, and decomposes at higher temperatures; it reduces ammoniacal silver nitrate on prolonged boiling, gives the murexide coloration with concentrated hydrochloric acid, and is hydrolysed to monoacetyldiaminouracil,  $\text{C}_6\text{H}_8\text{O}_3\text{N}_4$ , by alkali hydroxides. A triacetyl derivative,  $\text{C}_{10}\text{H}_{12}\text{O}_5\text{N}_4$ , is also formed in the condensation, but is hydrolysed to the diacetyl compound by the action of water; the total yield of the latter substance is 75 per cent. of the uric acid employed.

G. T. M.

Homologues of Xanthine. C. F. BOEHRINGER & SÜHNE (D.R.-P. 128212).—1:3:7:8-Tetramethylxanthine (8-methylcaffeine), prepared by heating 8-methylxanthine, 3:8-dimethylxanthine, or 1:3:8-trimethylxanthine with methyl iodide and 2*N*-sodium or potassium hydroxide solution for 4 to 7 hours at 80°, crystallises from water or the ordinary organic solvents in concentric aggregates of lustrous needles sintering at 205° and melting at 207—208.5°; at higher temperatures, it volatilises without decomposition.

3:7:8-Trimethylxanthine, produced by heating the dry barium, lead, or dipotassium derivative of 8-methylxanthine with an ethereal solution of methyl iodide at 120—123° for 60 hours, crystallises from water in lustrous needles and from alcohol in short, thick prisms; it dissolves in acid and alkali solutions, and yields a sodium derivative separating in slender, felted needles. The base sinters at 296° and melts at 302—303°; it sublimes without decomposition.

7-Benzyl-1:3:8-trimethylxanthine, obtained by the action of benzyl chloride and alcoholic sodium hydroxide solution on 1:3:8-trimethylxanthine, crystallises in clusters of needles melting at 159—160.5°.

8-Methyl-1:3:7-triethylxanthine, prepared from 8-methylxanthine by the action of ethyl iodide and sodium hydroxide, crystallises in vitreous prisms sintering at 128° and melting at 132—133°.

1:3:7-Trimethyl-8-ethylxanthine forms needles melting at 186—187·5°; triethylxanthine separates in hexagonal plates, sintering at 195° and melting at 210—212°. G. T. M.

**Thioxanthine.** C. F. BOEHRINGER & SÖHNE (D.R.-P. 128117. Compare Abstr., 1898, i, 340).—Thioxanthine (2:6-dioxy-8-thiopurine) may be prepared by heating the alkali urates in aqueous solution or suspension with carbon disulphide at 150°. G. T. M.

**Synthesis of Methylrubazonic Acid.** By FR. PRÖSCHER (*Ber.*, 1902, 35, 1436—1437).—Methylrubazonic acid can be prepared by the condensation of nitrosoantipyrine with phenylmethylpyrazolone. Nitrosoantipyrine also condenses with pyrrole and other bases to form indamine dyes. T. M. L.

**Spontaneous Decomposition of Nitrosobenzene.** By EUGEN BAMBERGER (*Ber.*, 1902, 35, 1606—1614).—When nitrosobenzene in solution in dry benzene is exposed to sunlight, it rapidly decomposes, forming mainly azoxybenzene, together with small quantities of nitrobenzene, aniline, *o*-hydroxyazobenzene and *o*-hydroxyazoxybenzene, and traces of quinol, *iso-o*-hydroxyazoxybenzene, *p*-hydroxyazoxybenzene, and other substances. The same decomposition takes place, only far more slowly, in the absence of light. When heated alone or in solution in petroleum, nitrosobenzene yields the same products. With the exception of quinol, the substances just mentioned are obtained by the action of sodium hydroxide on nitrosobenzene (Abstr., 1900, i, 531) and are separated in the manner previously described.

The opinion is expressed that in this decomposition nitrosobenzene is first converted into a mixture of phenylhydroxylamine and nitrobenzene; the former then, with unchanged nitrosobenzene, yields azoxybenzene. On the other hand, phenylhydroxylamine, under the same conditions, forms nitrosobenzene and aniline, the former with unchanged phenylhydroxylamine producing azoxybenzene (Abstr., 1900, i, 221). K. J. P. O.

**Hydroxyazoxybenzenes.** By EUGEN BAMBERGER (*Ber.*, 1902, 35, 1614—1623).—An investigation of *o*-hydroxyazoxybenzene (m. p. 75·5—76°) and *iso-o*-hydroxyazoxybenzene (m. p. 108—108·5°) (Abstr., 1900, i, 531) has shown that they both have a mol. weight, represented by the formula  $C_{12}H_{10}O_2N_2$ ; both dissolve in aqueous sodium hydroxide, are reduced by zinc and ammonium chloride to a mixture of *o*-aminophenol and aniline, and by concentrated sulphuric acid are converted into *o*-hydroxyazobenzene.

*o*-Acetoxyazoxybenzene,  $C_6H_5 \cdot N_2O \cdot C_6H_4 \cdot OAc$ , prepared from acetic anhydride and *o*-hydroxyazoxybenzene, crystallises in lustrous, straw-yellow prisms melting at 56—57°; the acetyl derivative of the *iso*-compound was not obtained in a pure state.

*Benzeneazo-o-hydroxyazoxybenzene*,  $N_2Ph \cdot C_6H_3(OH) \cdot N_2O \cdot Ph$ , is formed by the action of benzenediazonium acetate on *o*-hydroxyazoxy-

benzene or on the *iso*-compound (?); it crystallises in pale orange-yellow needles melting at 145—145.5°, and dissolves in alkali hydroxides with a bordeaux-red coloration. It is thought that these two substances are possibly stereoisomeric.

The *p*-hydroxyazoxybenzene (m. p. 145°) obtained by Kekulé and Hidegh (*Ber.*, 1870, 3, 235) by the action of phosphorus pentachloride on *p*-hydroxyazobenzene, is not identical with the compound (m. p. 156—156.5°) prepared from nitrosobenzene by the author (*loc. cit.*). As Kekulé and Hidegh's substance is not soluble in alkali hydroxides and is not oxidised by permanganate, it does not bear the same relation to the author's *p*-hydroxyazoxybenzene that *o*-hydroxyazoxybenzene bears to *iso-o*-hydroxyazoxybenzene. K. J. P. O.

**Synthesis of *p*-Hydroxyazoxybenzene.** By EUGEN BAMBERGER and WALTHER BERNAYS (*Ber.*, 1902, 35, 1624—1626. Compare preceding abstracts).—*p*-Hydroxyazoxybenzene was synthesised by condensing phenylhydroxylamine and *p*-nitrosophenol, and was identical with the substance previously obtained by the decomposition of nitrosobenzene (*Abstr.*, 1900, i, 531). The yield of *p*-hydroxyazoxybenzene was very small; purification was only effected by repeated fractional precipitation of the ammoniacal solution with carbon dioxide. K. J. P. O.

**Reduction Products of the Nitronaphthalenes.** By LEONHARD WACKER (*Annalen*, 1902, 321, 61—70. Compare *Abstr.*, 1901, i, 655).— $\alpha$ -Nitronaphthalene, when reduced either with dextrose or phenylhydrazine and alcoholic sodium hydroxide solution, yields a yellow compound melting at 120°, and probably having the formula  $C_{20}H_{12}ON_2$ . 5:5'-Dinitroazoxynaphthalene,  $ON_2(C_{10}H_6 \cdot NO_2)_2$ , obtained by reducing 1:5-dinitronaphthalene with zinc dust and ammonium chloride or phenylhydrazine and sodium hydroxide, is orange-yellow and decomposes above 200°. 1:1'-Azoxynaphthalene-5:5'-disulphonic acid is readily obtained from sodium 1:5-nitronaphthalenesulphonate by reduction with dextrose and aqueous sodium hydroxide solution; it is isolated in the form of its sodium salt,  $C_{20}H_{12}O_7N_2S_2Na_2 \cdot 2H_2O$ , which crystallises from water in prisms or leaflets. Hydroxyazonaphthalene-5:5'-disulphonic acid, produced by dissolving the preceding sodium salt in 90—93 per cent. sulphuric acid at 35°, is isolated as the ammonium salt,  $C_{20}H_{20}O_7N_4S_2$ . Azoxynaphthalene-3:8:3':8'-tetrasulphonic acid, prepared by reducing sodium  $\alpha$ -nitronaphthalene-3:8-disulphonate with dextrose and aqueous sodium hydroxide solution at 50°, is obtained in the form of its yellow potassium salt,  $ON_2[C_{10}H_5(SO_3K)_2]_2$ , this substance separating from aqueous solutions of the acid on adding excess of potassium hydroxide. This azoxynaphthalenetetrasulphonic acid is not readily transformed into a hydroxyazo-compound, but the sulphonic acids of  $\alpha$ -nitronaphthalene containing the sulphonic acid groups in positions 6, 7, and 8 are readily reduced, and easily undergo this transformation. G. T. M.

**Action of the Malonic Esters on Diazonium and Tetrazonium Chlorides.** By G. FAVREL (*Bull. Soc. Chim.*, 1902, [iii], 27, 313—323).—By the action of ethyl malonate on diphenyltetraz-

azonium chloride in acetic acid solution, *ethyl diphenyldihydrazone-malonate*,  $C_{12}H_8[NH \cdot N \cdot C(CO_2Et)_2]_2$ , is obtained, which crystallises in small, lustrous, yellow plates melting at  $178-180^\circ$ ; it readily dissolves in alcohol, benzene, toluene, xylene, nitrobenzene, or aniline, but is insoluble in aqueous or alcoholic solutions of the alkalis. When acted on by sodium ethoxide, the *disodium* derivative is obtained as a reddish, crystalline powder; when this is acted on by alkyl iodides or by acyl chlorides, no alkyl or acyl derivatives of ethyl diphenyldihydrazone-malonate are obtained. *Diphenyldihydrazone-malonic acid* is a clear yellow powder insoluble in the ordinary solvents in the cold; on warming, it decomposes; it has not been found possible to prepare the hexa-sodium derivative of the acid. *Methyl diphenyldihydrazone-malonate*, obtained in a similar manner to the ethyl ester, forms small, yellow crystals which melt at  $217-220^\circ$ ; it is insoluble in alcohol or ether. *Ethyl di-o-tolyldihydrazone-malonate*, obtained from ethyl malonate and ditolyltetrazonium chloride, forms small, orange-red crystals which melt at  $188-190^\circ$ , and are sparingly soluble in alcohol, but much more so in toluene, xylene, nitrobenzene, aniline, chloroform, or acetone. Its disodium derivative forms small red crystals. *Di-o-tolyldihydrazone-malonic acid* is much more stable than diphenyldihydrazone-malonic acid, and can be obtained in small, orange-coloured plates which decompose without melting at  $195-200^\circ$ . The *methyl* ester of this acid crystallises from nitrobenzene in bundles of small, reddish crystals which melt at  $210-212^\circ$ . *Ethyl di-o-anisyl-dihydrazone-malonate* forms orange-coloured crystals melting at  $190-192^\circ$ , the *methyl* ester separates from hot aniline in yellow crystals which melt at  $268-270^\circ$ .

The foregoing compounds are probably all to be regarded as dihydrazones of mesoxalic acid or its esters (compare Meyer, Abstr., 1891, 922). A. F.

**Action of Substituted Malonic Esters on Diazonium Chlorides.** By G. FAVREL (*Bull. Soc. Chim.* 1902, [iii], 27, 324-328).—By the action of diazonium chlorides on substituted malonic esters, hydrazones of ketonic acids are obtained, with production of alcohol and elimination of carbon dioxide. In this way, the author has prepared the phenylhydrazone and *p*-tolylhydrazone of ethyl pyruvate, and the phenylhydrazone and the *o*-tolylhydrazone of  $\alpha$ -keto-butyric acid, the latter compound melting at  $156^\circ$ . A. F.

**Action of Acetylacetone and of its Substituted Derivatives on Diazonium and Tetrazonium Chlorides.** By G. FAVREL (*Bull. Soc. Chim.*, 1902, [iii], 27, 328-336).—By the action of diphenyltetrazonium chloride on acetylacetone, there is obtained *acetylacetone diphenyldihydrazone* ( $\beta\delta$ -pentanedione- $\gamma$ -diphenyldihydrazone,  $CAc_2 \cdot N \cdot NH \cdot C_6H_4 \cdot C_6H_4 \cdot NH \cdot N \cdot CAc_2$ ; it is insoluble in the ordinary solvents but dissolves in boiling aniline or nitrobenzene, from which it separates in small, reddish crystals melting at  $258-260^\circ$ . It is very stable, and is decomposed only by fusing with alkali hydroxides; it does not react with phenylhydrazine. Its *sodium* derivative crystallises from acetone or pyridine in small, reddish crystals.

If mol. proportions of acetylacetone and diphenyltetrazonium chloride are allowed to interact in acetic acid solution, a substance which is probably *cyclodiphenylformazyl methyl ketone*, is produced.

*Acetylacetonedi-phenyldimethylhydrazone* ( $\beta\delta$ -*pentanedione- $\gamma$ -diphenyldimethylhydrazone*), obtained by the action of methyl sulphate on sodioacetylacetonedi-phenyldihydrazone, separates from its alcoholic solution in small, reddish crystals which melt at 168—170°.

*Acetylacetonedi-o-tolyldihydrazone* ( $\beta\delta$ -*pentanedione- $\gamma$ -di-o-tolyldihydrazone*), obtained in a similar manner to the preceding analogous compounds, forms small, red needles which melt at 250—252°, and are insoluble in the ordinary solvents but soluble in hot aniline or nitrobenzene. Its *disodium* derivative forms small, red, lamellar crystals, insoluble in water or alcohol, soluble in acetone or in pyridine.

*Acetylacetonedi-o-tolyldimethylhydrazone* ( $\beta\delta$ -*pentanedione-di-o-tolyldimethylhydrazone*), obtained by heating the preceding disodium compound with methyl sulphate, forms small, red, silky crystals melting at 247—248°.

*Acetylacetonedi-o-anisylidihydrazone* ( $\beta\delta$ -*pentanedione- $\gamma$ -di-o-anisylidihydrazone*), forms slender, scarlet-coloured needles which melt at 234—235°. *Sodioacetylacetonedi-o-anisylidihydrazone* crystallises from pyridine in very light, small red needles.

*Acetylacetonedi-o-anisylldimethylhydrazone* ( $\beta\delta$ -*pentanedione- $\gamma$ -di-o-anisylldimethylhydrazone*), crystallises from chloroform in small, red needles which melt at 257—258°.

A. F.

**Action of Alkylacetylacetones on Diazonium and Tetrazonium Chlorides.** By G. FAVREL (*Bull. Soc. Chim.*, 1902, [iii], 27, 336—342).—By the action of benzenediazonium chloride on methylacetylacetone in acetic acid solution, diacetylmonophenylhydrazone is obtained. Similarly, by the action of *p*-toluenediazonium chloride on methylacetylacetone, there is obtained *diacetylmono-p-tolyldihydrazone*, which forms small, yellowish crystals melting at 119—120°, and with *o*-toluenediazonium chloride, *diacetylmono-o-tolyldihydrazone*, which forms crystals of a clear yellow colour melting at 130—131°.

Further, by adding solutions of diphenyltetrazonium chloride and di-o-tolyltetrazonium chloride to alcoholic solutions of methylacetylacetone, *diacetyldiphenyldihydrazone*, melting at 283—284°, and *di-o-tolyldihydrazone*, melting at 240—242° respectively, are obtained.

By acting on ethylacetylacetone with diazonium and tetrazonium chlorides, corresponding derivatives of propionylacetyl are obtained. The *propionylacetylmono-p-tolyldihydrazone* ( $\beta\gamma$ -*pentanedione- $\gamma$ -p-tolyldihydrazone*) forms small, orange-coloured crystals melting at 137—138°, and *propionylacetylmono-o-tolyldihydrazone* ( $\beta\gamma$ -*pentanedione- $\gamma$ -o-tolyldihydrazone*) forms pale yellow coloured crystals melting at 58—60°. *Propionylacetyldiphenyldihydrazone* ( $\beta\gamma$ -*pentanedione- $\gamma$ -diphenyldihydrazone*), obtained by the action of diphenyltetrazonium chloride on ethylacetylacetone, crystallises from nitrobenzene or aniline in red coloured crystals melting at 292—294°.

A. F.

**Action of Hydrazine Bases on "Quinols" [ $\psi$ -Quinols].** Notes on the History of "Quinols." By EUGEN BAMBERGER (*Ber.*, 1902, 35, 1424—1431).—The products obtained by the interaction of  $\psi$ -quinols with *p*-nitrophenylhydrazine and with semicarbazide are azo-compounds of the type  $\text{Alk}\cdot\text{C}\begin{smallmatrix} \diagup \text{C} \diagdown \\ \diagdown \text{C} \diagup \end{smallmatrix}\text{C}\cdot\text{N}\cdot\text{NR}$ , instead of being cyclic

anhydrides,  $\text{Alk}\cdot\text{C}\begin{smallmatrix} \diagup \text{C} \diagdown \\ \diagdown \text{C} \diagup \\ \text{NR}\cdot\text{N} \end{smallmatrix}\text{C}$ , as previously considered (Abstr., 1901, i, 140).

The interaction of 1-hydroxy-4-ketotoluene with phenylhydrazine yields *p*-tolueneazobenzene, identical with the substance obtained by the interaction of nitrosobenzene and *p*-toluidine (Mills, *Trans.*, 1895, 67, 929); the azo-compound melts at 69.5—70.5°, and sublimes between 80° and 90° in orange leaflets. By using *p*-nitrophenylhydrazine, *p*-tolueneazo-*p*-nitrobenzene,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , is obtained; it crystallises in red, lustrous, felted needles and melts at 181°.

The interaction of 1-hydroxy-4-ketotoluene with semicarbazide yields *p*-tolueneazocarbonamide,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_2\cdot\text{CO}\cdot\text{NH}_2$ , which crystallises from water in orange-red leaflets or flat needles with a bronze lustre, melts at 141.5—142°, and can also be obtained by oxidising *p*-tolylsemicarbazide,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , with aqueous potassium permanganate; the latter is formed by the action of potassium cyanate on *p*-tolylhydrazine in aqueous solution and crystallises in silky, white leaflets or flat needles and melts at 190—191°.

A note as to the history of the "quinols" is appended. W. A. D.

**Electrochemical Reduction of 2:2'-Dinitrodiphenyl to Phenazone and Derivatives of the Latter.** By TH. WOHLFAHRT (*J. pr. Chem.*, 1902, [ii], 65, 295—299).—2:2'-Dinitrodiphenyl gives a 95 per cent. yield of phenazone when electrolysed under the following conditions:—anode, lead strips in a cold saturated solution of sodium carbonate; cathode, a cylinder of nickel gauze of 250 sq. cm. area immersed in a solution of 10 grams of the substance in 200 c.c. of alcohol with 30 c.c. of water and 2 grams of sodium acetate and cathode density of 5—6 amperes per sq. decm.

*Methylphenazone methyl sulphate*, obtained by heating phenazone with an excess of methyl sulphate at 80—100°, separates from alcohol in very hygroscopic, yellow needles, and when heated with potassium iodide, yields *phenazone methiodide* which separates from glacial acetic acid in dark-red crystals, darkens at 100° and melts at 185—187°. *Methylphenazone platinichloride* crystallises in lustrous yellow leaflets.

*Phenazone ethiodide*, obtained by the action of ethyl iodide on phenazone, separates from an alcoholic solution on the addition of ether and melts at 185—187°. R. H. P.

**Compounds of Sodium Tetrazoditolylsulphonate with Aromatic Amines and Phenols, and their Conversion into Azo-colours.** By ALPHONSE SEYEWETZ and BIOT (*Compt. rend.*, 1902, 134, 1068—1070).—When aqueous solutions of sodium tetrazoditolylsulphonate and an aromatic amine are mixed, colourless, crystalline

compounds are produced which become coloured by the action of light or by prolonged boiling with alcohol. Compounds have been obtained from aniline and the toluidines; they decompose at 160°, are little soluble in water or cold alcohol, insoluble in ether, benzene, or chloroform, but easily soluble in hot alcohol. Diamines react precisely in the same way as monoamines, as has been proved with *p*-phenylenediamine. Similar compounds have also been prepared with  $\alpha$ - and  $\beta$ -naphthylamine and  $\alpha$ -ethylnaphthylamine.

Two molecules of the amine react with one molecule of the tetrazo-compound, and a colourless hydrazine compound is formed. Thus, in the case of naphthylamine (hydrochloride) the reaction is represented:  $\text{NaSO}_3 \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{N} \cdot \text{N} \cdot \text{SO}_3\text{Na} + 2(\text{C}_{10}\text{H}_7\text{NH}_2, \text{HCl}) = 2\text{NaCl} + \text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{N}(\text{SO}_3\text{H}) \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH} \cdot \text{N}(\text{SO}_3\text{H}) \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH}_2$ . The coloured substance is produced from this hydrazine derivative according to the equation  $\text{C}_{34}\text{H}_{32}\text{O}_6\text{N}_6\text{S}_2 = 2\text{SO}_2 + 2\text{H}_2\text{O} + \text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{N} \cdot \text{N} \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH}_2$ . That the substances contain amino-groups is proved by the fact that they can be diazotised.

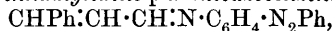
J. McC.

**Derivatives of *p*-Aminoazobenzene.** By MARYAN WIELEŻYŃSKI (*Ber.*, 1902, 35, 1431—1433).—*Methoxalylaminoozobenzene*,



obtained by heating methyl oxalate and aminoazobenzene, crystallises from benzene in orange-yellow leaflets and melts at 178—179°. *Succinyl-p-aminoazobenzene*,  $\text{C}_2\text{H}_4(\text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2\text{Ph})_2$ , prepared from succinyl chloride and the base, crystallises from amyl acetate and melts at 221—222°. *Benzoyl-p-aminoazobenzene* crystallises from glacial acetic acid in golden leaflets and melts at 205°. *Phthalyl-p-amino-*

*azobenzene*,  $\text{C}_6\text{H}_4 \cdot \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2\text{Ph}$ , prepared by using phthalyl chloride, crystallises from glacial acetic acid in flesh-coloured crystals melting at 250°. *Cinnamylidene-p-aminoazobenzene*,



obtained by means of cinnamaldehyde, crystallises from alcohol in small, orange-yellow crystals and melts at 136°; *vannillylidene-p-aminoazobenzene* forms small, dark red crystals and melts at 157°.

Formaldehyde combines with *p*-aminoazobenzene to yield the *derivative*,  $\text{CH}_2 \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2\text{Ph}$ , melting at 196—200°, but acetaldehyde, acetone, and ænanthaldehyde are without action.

W. A. D.

**Conversion of Hydrazobenzene into Benzidine by Glacial Acetic Acid.** By FRANZ SACHS and CROYDEN M. WHITTAKER (*Ber.*, 1901, 35, 1433—1435. Compare Rassow and Rülke, this vol., i, 404).—The conversion of hydrazobenzene into benzidine can be brought about by organic acids if some substance is present to combine with the benzidine as fast as it is formed. Thus when heated with acetic acid and *p*-dimethylaminobenzaldehyde, hydrazobenzene is completely converted into bis-*p*-dimethylaminobenzylidenbenzidine,  $\text{C}_{12}\text{H}_8(\text{N} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ ; this base, which has not previously been prepared in a pure state, is a yellow powder which can be crystallised from nitrobenzene and melts at 317°.



By boiling with acetic acid alone, hydrazobenzene was converted into diacetylbenzidine, which melts at 329—331° (corr.) and not at 317°.  
T. M. L.

**Action of Nascent Chlorine on Proteids.** By R. EHRENFELD (*Zeit. physiol. Chem.*, 1902, **34**, 566—579. Compare Abstr., 1901, i, 622).—Egg-albumin, serum-albumin, vitellin, legumin, and other proteids react with nascent chlorine in very much the same manner as casein, and the chlorinated products obtained resemble proteids in both physical and chemical properties. When moist, they dissolve in alcohol containing a little hydrochloric acid and in acetic acid, also in alkali hydroxides in aqueous ammonia. The percentage composition of the different products varies considerably. The chlorine derivative from egg-albumin contains 6.51, that from serum-albumin 8.95, that from vitellin 10.0, from legumin 9.63 and from gluten (?) 4.81 per cent. of chlorine, and all appear to be free from sulphur. J. J. S.

**Compounds of Proteids with Metaphosphoric Acid.** By ERNST FULD (*Beitr. chem. Physiol. Path.*, 1902, **2**, 155—168).—A method is described by means of which compounds of proteid and metaphosphoric acid of constant composition can be prepared. The proteids used were crystallised serum-albumin, crystallised egg-albumin, casein, and edestin. The amount of phosphorus is different in the various proteid meta-phosphates. Of the proteoses, hetero-proteose was the only one which gives a well marked precipitate with metaphosphoric acid.  
W. D. H.

**Formation of Glycogen from Proteid.** By ERNST BENDIX (*Zeit. physiol. Chem.*, 1902, **34**, 544—548).—A reply to Schöndorff (this vol., ii, 154).  
J. J. S.

**Pseudo-mucin.** By CARL NEUBERG and FELIX HEYMANN (*Beitr. chem. Physiol. Path.*, 1902, **2**, 201—213).—Leathes has shown that by peptic digestion the viscid substance known as paramucin passes into the easily soluble form (pseudo-mucin). Both these ovarian mucoids resemble mucin in their glucoside character. In the true mucins, the reducing material appears to be a substance which yields glucosamine (chitosamine). Concerning the nature of the carbohydrate group in ovarian mucoid, three opinions have been recently expressed. Panzer (Abstr., 1900, i, 70) considers it to be an ethereal sulphate allied to chondroitin-sulphuric acid, which by hydrolysis yields glucosamine and a pentose. Leathes (Abstr., 1900, i, 318) names the reducing material paramucosin; this is regarded as a reduced chondrosin (anhydro-chitosamine-glycuronic acid); on hydrolysis, it yields gulose and chitosamine. Zangerle (*Münch. med. Woch.*, 1900, 214) obtained a crystalline benzoate of an amino-sugar; this benzoate, when hydrolysed, yielded, with hydrochloric acid, a substance crystallographically identified as glucosamine hydrochloride. In the present research, a fourth result is arrived at. Pseudo-mucin was decomposed by fuming hydrobromic acid, and after further treatment a compound of cinchonine was obtained with the composition

of cinchonine *noris*osaccharate. According to Fischer and Tiemann, *noris*osaccharic acid is only obtainable from chitin and glucosamine. It is therefore proved that pseudo-mucin contains a glucosamine-yielding group in important quantities. No other carbohydrate substance is present. Gulose, which according to Leathes enters into the composition of paramucin, was not found. W. D. H.

**Hydrolysis of Gelatin.** By EMIL FISCHER, P. A. LEVENE, and R. H. ADERS (*Zeit. physiol. Chem.*, 1902, 35, 70—79. Compare Abstr., 1901, i, 780).—Gelatin was hydrolysed by heating for several hours with hydrochloric acid, and the amino-acids thus formed converted into esters (Abstr., 1901, i, 192). On saturating the alcoholic solution of the esters with hydrogen chloride, glycine may be completely separated as the hydrochloride of the ester. The esters of the amino-acids contained in the mother liquid are separated by fractionation under a pressure of 8—10 mm.; the first fraction (b. p. 40—55°) contained mainly the ester of *D*-alanine, the second (b. p. 55—80°) that of *L*-pyrrolidine-2-carboxylic acid, the third (80—100°) the ethyl ester of *L*-leucine, together with the last-mentioned ester, the fourth (b. p. 100—130°) ethyl aspartate, together with other substances, the fifth (b. p. 130—160°) the esters of *D*-phenylalanine, and *D*-glutamic acid. On hydrolysing the esters, the active acids were always partially racemised. Glycine represents 16·5 per cent. of the dry gelatin, alanine 0·8, pyrrolidinecarboxylic acid 5·2, leucine 2·1, aspartic acid 0·56, glutamic acid 0·88, and phenylalanine 0·4 per cent. Amino-valeric acid is also probably formed, and possibly aminobutyric acid.

K. J. P. O.

**Dissociation and Combination of Witte's Peptone.** By TORALD SOLLMANN (*Amer. J. Physiol.*, 1902, 7, 203—219).—Data are given relating to the reaction of Witte's peptone towards different indicators, the composition of the ash, the dissociability of the pure albumose solution, the combination of Witte's peptone with sulphuric acid, and the combination of albumose with sodium hydroxide. Witte's peptone has an average mol. weight of 630, but is dissociable into four molecules by dilution. By heat, an alkaline molecule is eliminated; it appears to be univalent towards acids or bases. W. D. H.

**Hydrolysis of Acid Amides and Anilides by Ferments.** By MAX GONNERMANN (*Plüger's Archiv*, 1902, 89, 493—516).—Experiments were carried out with the following amides and anilides: formamide, acetamide, oxamide, succinamide, benzamide, salicylamide, formanilide, acetanilide, oxanilide, and benzanilide. Of these, formanilide and acetanilide are hydrolysed by pepsin; acetamide, formanilide, and acetanilide by trypsin; acetamide and formanilide by emulsin. Ptyalin, invertin, and maltin have no action on any of these substances. The finely divided liver of the sheep brings about the hydrolysis of formamide, acetamide, succinamide, benzamide, and formanilide, whilst the finely divided kidneys of the sheep bring about the hydrolysis of formamide, benzamide, salicylamide, formanilide, and benzanilide. The results obtained with these two organs agree with

those obtained by various workers in experiments made on living animals. All the experiments were carried out in presence of 1 per cent. of sodium fluoride to prevent bacterial action.

The aqueous solution of acetamide has an acid reaction. Acetamide readily volatilises when its aqueous solution is evaporated. "Pure" oxamide was found in some cases to contain a large amount of oxalic acid. Salicylic acid is readily soluble in concentrated ammonium acetate solution and can thus be separated from the amide, which is insoluble. A. H.

**An Important Source of Error in the Examination of Diastases.** By M. EMM. POZZI-ESCOT (*Compt. rend.*, 1902, 134, 479—480).—The white, aqueous emulsion of guaiacum resin, when mixed with a few drops of hydrogen peroxide, developed a blue coloration in the presence of oxydases and other diastases. This reaction is, however, by no means general for all classes of diastases.

The diastases from *Aspergillus oryzae* and *Penicillium glaucum*, and the hydrogenases which are identical with catalase (Loew, Abstr., 1901, i, 435), all energetically decompose hydrogen peroxide, but do not yield the blue coloration with guaiaconic acid; this anomaly is due to the reducing action of the hydrogenases. The presence of these enzymes would therefore suffice to mask that of any oxydases in a mixture of diastatic ferments. G. T. M.

**Differences between Diastases.** By HORACE M. VERNON (*J. Physiol.*, 1902, 28, 156—174).—The progress of the colour reactions with dilute iodine during the progress of starch digestion varies considerably according to the nature of the diastase employed. The different diastases of animal and vegetable origin are therefore considered to be different substances. W. D. H.

**Catalytic Properties of the Hydrogenases; Identification of Loew's "Catalase" with De Rey-Pailhade's "Philothion."** By M. EMM. POZZI-ESCOT (*Bull. Soc. Chim.*, 1902, [iii], 27, 280—288).—Philothion (compare Abstr., 1888, 1101) does not give a blue coloration with tincture of guaiacum and hydrogen peroxide, the usual reaction of the diastases. It decomposes hydrogen peroxide, however, the amount of oxygen liberated being proportional to the amount of philothion employed, and the velocity of decomposition being a function only of the "active mass." The amount of oxygen evolved is at first comparatively large, but gradually diminishes, and at last the evolution of gas ceases; the maximum action takes place at a temperature between 30° and 40°. The action does not appear to be purely catalytic, but rather chemical, and at length ceases owing to the oxidation of the hydrogenase. The action of "paralysing" or retarding substances on the reaction was also studied, and it was found that mercuric chloride and silver nitrate are exceedingly powerful retarders, and generally that salts with an acid reaction have the most powerful retarding effect, whilst alkalis have an accelerating action.

On account of the agreement between philothion and catalase (compare Abstr., 1901, i, 435) with regard to the decomposition of hydrogen

peroxide, the action of salts on that decomposition, and other properties, such as the production of hydrogen sulphide from sulphur, the author concludes that philothion and catalase are identical. He is not able to confirm Loew's statement as to the oxidation of quinol by means of catalase.

A. F.

**Phenolphthalin as a Reagent for the Oxidising Ferments.** By J. H. KASTLE and O. M. SHEDD (*Amer. Chem. J.*, 1901, 26, 526—539).—The oxidation of phenolphthalin to phenolphthalein by the oxidising ferment of potato extract has been investigated. The reaction was carried out in acid solution and the depth of colour developed on adding alkali served as a guide to the extent of oxidation which had taken place. An aqueous solution of the oxydase of potato loses its oxidising property on standing. The oxydase is distributed throughout the whole of the potato, the hypodermal layer being possibly richest in it. The oxidation is apparently effected by the oxydase itself, and this does not seem to act simply as an oxygen-carrier. The action of the oxydase proceeds slowly, and phenolphthalin is an excellent reagent for following its course; the reaction reaches its maximum at about the end of an hour.

The particular oxydase which turns guaiacum resin blue directly and oxidises phenolphthalin, is not confined to the potato, but is widely distributed in the vegetable kingdom and occurs also in human saliva. The oxydase is probably not identical with the catalase described by Loew (U.S. Dept. Agric., Report No. 68).

J. McC.

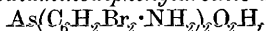
**Nature of certain of the Oxidising Ferments.** By J. H. KASTLE and A. S. LOEVENHART (*Amer. Chem. J.*, 1901, 26, 539—566).—Guaiacum becomes blue immediately when added to a potato the skin of which has been removed, but the blue colour only appears on standing when the guaiacum is applied to the interior pulp of the potato. The oxidising substance of the potato is unstable, but its stability can be increased by certain antiseptics (chloroform or thymol). Schönbein's observation that atmospheric oxygen is essential for the formation of guaiacum-blue by the oxygen-carrier of the potato has been definitely confirmed. Organic peroxides (for example, benzoyl peroxide) give an immediate blue coloration with guaiacum. The oxidising substance of the potato is very easily soluble in water, but is insoluble in ethyl or amyl alcohol. Various substances (particularly hydrocyanic acid, salicylic acid, hydroxylamine, phenylhydrazine, and sodium thiosulphate) inhibit the turning blue of guaiacum by potato extract; silver nitrate and mercuric chloride seem to be without influence. The same substances which inhibit the reaction of the potato extract exert a similar influence on the turning blue of guaiacum by peroxides (both organic and inorganic), and this, coupled with the inactivity of silver and mercuric salts, leads the authors to conclude that the oxidising substance of the potato is not a true soluble ferment but an organic peroxide. They explain its action by Baeyer and Villiger's theory (*Abstr.*, 1900, i, 437); it acts as a carrier of oxygen in the same way that benzaldehyde does, but is not a true catalytic agent. Nothing definite can be said of the nature of the substance, but it may possibly be an aldehyde.

J. McC.

**Aromatic Arsenic Compounds.** By AUGUST MICHAELIS (*Annalen*, 1902, 321, 141—248. Compare this vol., i, 411).—[With W. WEBER.]—Diphenylchloroarsine,  $\text{AsPh}_2\text{Cl}$  (b. p.  $333^\circ$ ), prepared either by heating phenylchloroarsine and mercury diphenyl or by distilling triphenylarsinedichloride, yields diphenylarsinic acid,  $\text{AsPh}_2\text{O}\cdot\text{OH}$ , when oxidised by chlorine water. The acid, which can also behave as a base, yields the *nitrate*,  $\text{AsPh}_2\text{O}\cdot\text{ONO}_3$ , on treatment with a cold mixture of concentrated nitric and sulphuric acids; this derivative separates from glacial acetic acid in white needles and melts at  $125^\circ$ ; it is insoluble in the other organic solvents.

*Dinitrodiphenylarsinic acid*,  $\text{As}(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2\text{O}\cdot\text{OH}$ , resulting from the action of the heated mixed acids, crystallises from glacial acetic acid in yellow prisms and melts at  $256^\circ$ ; it is very sparingly soluble in water, alcohol, benzene, chloroform, or ether. The salts of the alkalis and alkaline earth metals are easily soluble, the *barium* salt crystallises in pale yellow flakes, the normal *silver* salt is a white precipitate, the *copper* salt has the composition  $(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2\text{AsO}\cdot\text{OCu}\cdot\text{OH}$ .

The preceding nitro-acid does not yield amino-derivatives on reduction, but *tetrabromodiaminodiphenylarsinic acid*,



melting indefinitely at  $187^\circ$ , is obtained by heating diaminodiphenyl sulphide with bromine water on the water-bath; at higher temperatures the *hexabromodiaminodiphenylarsinic acid* is produced; this substance is a very stable, white powder melting at  $287^\circ$ .

*Tetranitrotetraphenyldiarsine*,  $\text{As}(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2\cdot\text{As}(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ , prepared by heating a glacial acetic acid solution of dinitrodiphenylarsinic acid with phosphorous acid, separates on cooling in lustrous leaflets and melts at  $200^\circ$ ; the *tetra-amino*-compound resulting from the prolonged action of the reducing agent is amorphous; its *tetra-acetyl* derivative, a white pulverulent substance, melts at  $162^\circ$ . Tetraphenyldiarsine is similarly produced from diphenylarsenous oxide.

*Dinitrodiphenylchloroarsine*,  $\text{As}(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2\text{Cl}$ , is produced by passing chlorine into a benzene solution of tetranitrotetraphenyldiarsine; a *trichloride* is simultaneously formed which changes into the monochloride on adding to the solution an excess of the tetranitro-compound. The monochloride crystallises in pale yellow needles and melts at  $112^\circ$ ; it dissolves in alkaline solutions, yielding salts of dinitrodiphenylarsenious acid.

*Dinitrodiphenylbromoarsine*,  $\text{As}(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2\text{Br}$ , forms transparent, colourless leaflets melting at  $93^\circ$ . The *tribromoarsine*,  $(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2\text{AsBr}_3$ , is a solid substance readily decomposed by moisture, yielding dinitrodiphenylarsinic acid.

Diphenylarsenious acid is not stable, but its *phenyl ester*,  $\text{AsPh}_2\cdot\text{OPh}$ , is a colourless liquid boiling at  $230\text{--}231^\circ$  under 15 mm. pressure, and having a sp. gr. 1.3113 at  $11^\circ$ ; it solidifies in a freezing mixture and is hydrolysed by water at  $100^\circ$  into phenol and diphenylarsenious oxide. This ester differs very materially from its isomeride, triphenylarsine oxide,  $\text{AsPh}_3\text{O}$ , the isomerism resembling that which obtains with the corresponding phosphorous compound.

*Phenoxydiphenylarsine chloride*,  $\text{AsPh}_2\text{Cl}_2\cdot\text{OPh}$ , obtained by passing chlorine into a petroleum solution of the phenyl ester, crystallises in

needles, melts at 121—122°, and is hydrolysed by water into diphenylarsinic acid, phenol, and hydrogen chloride. The corresponding *bromide*,  $\text{AsPh}_2\text{Br}_2\cdot\text{Oph}$ , forms yellowish-red crystals melting at 100°.

*Dinitrodiphenylarsenious acid*,  $\text{As}(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2\cdot\text{OH}$ , resulting from the action of water or alkaline solutions on dinitrodiphenylchloroarsine or the corresponding bromo-compound, crystallises from alcohol in white, felted needles, melts at 149°, and reduces silver nitrate; its salts are very unstable.

*Diphenylarsenious sulphide*,  $\text{S}(\text{AsPh}_2)_2$ , obtained by passing hydrogen sulphide in an alcoholic solution of diphenylarsenious oxide, crystallises from alcohol in white, silky needles melting at 67°; it is soluble in the ordinary organic solvents but not in aqueous solutions of the alkali hydroxides or monosulphides. Concentrated hydrochloric acid decomposes the sulphide, regenerating diphenylchloroarsine, the reverse change occurs slowly in warm alcoholic solution.

*Dinitrodiphenylarsenious sulphide*,  $\text{S}[\text{As}(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2]_2$ , separates, on adding alcohol to hot benzene solution of sulphur and tetranitrotetraphenyldiarsine, in aggregates of yellow needles melting at 156°. The *diamino*-derivative,  $\text{S}[\text{As}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2]_2$ , results from the action of a concentrated ammoniacal ammonium sulphide solution on the preceding compound and is isolated in the form of its hydrochloride on adding hydrochloric acid. The base is a white, amorphous powder and melts at 110°; the *sulphate*,  $\text{S}[\text{As}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2]_2\cdot 2\text{H}_2\text{SO}_4$ , separates from aqueous solutions in snow white needles; the *acetyl* derivative separates in flocculæ melting at 175°.

*Tetraphenylarsenic disulphide*,  $\text{S}_2(\text{AsPh}_2)_2$ , prepared by the action of ammoniacal ammonium sulphide solution on diphenylarsinic acid, is precipitated on adding hydrochloric acid, and crystallises from alcohol in white leaflets sintering at 60° and melting at 110°. *Tetranitrotetraphenylarsenic trisulphide*,  $\text{As}_2\text{S}_3(\text{C}_6\text{H}_4\cdot\text{NO}_2)_4$ , produced by boiling tetranitrotetraphenyldiarsine with sulphur suspended in benzene, is a yellow, crystalline substance melting at 69°.

[With H. PREDARI].—*Phenyl-p-tolylchloroarsine*,  $\text{C}_7\text{H}_7\cdot\text{AsPhCl}$ , prepared by boiling a mixture of phenylchloroarsine and mercurydi-p-tolyl, is a colourless, oily liquid, boiling at 215—237° under 29 mm. and at 215—240° under 50 mm. pressure; with chlorine, it yields a white, crystalline trichloride and with alcoholic potassium hydroxide a yellow, syrupy oxide,  $(\text{C}_7\text{H}_7\cdot\text{AsPh})_2\text{O}$ , the latter substance taking up chlorine to form an oxychloride,  $(\text{AsPh}\cdot\text{C}_7\text{H}_7)_2\text{OCl}_4$  crystallising in white needles.

*Phenyl-p-tolylarsenious sulphide*,  $(\text{C}_7\text{H}_7\cdot\text{AsPh})_2\text{S}$ , is an oil. *Phenyl-p-tolylarsinic acid*,  $\text{C}_7\text{H}_7\cdot\text{AsPh}\cdot\text{O}_2\text{H}$ , crystallises from water in felted, white needles and melts at 158—160°.

*Phenyl-p-tolylethylarsine*,  $\text{C}_7\text{H}_7\cdot\text{AsEtPh}$ , formed by the action of zinc ethyl, is a colourless oil having an unpleasant odour and boiling at 210—225° under 50 mm. pressure; the *dichloride*, formed by direct addition of chlorine, crystallises in white needles melting at 148°.

*Phenyl-p-tolylmethylethylarsonium iodide*,  $\text{C}_7\text{H}_7\cdot\text{AsMeEtPhI}$ , produced from methyl iodide and the preceding tertiary arsine, crystallises in white needles which, when deposited from water or alcohol, melt at 150—151° or at 145° respectively; the alcoholic solution of this asymmetric iodide has a slight optical rotation, but the salt could

not be resolved into its active components either by tartaric or aspartic acid, or by the action of fungi; the *chloride* is not crystalline but the *platinichloride* separates in yellowish-red, triclinic needles and melts at  $214^{\circ}$ .

*Phenyl-p-tolyldiethylarsonium iodide*,  $C_7H_7 \cdot AsPhEt_2I$ , crystallises from water in monoclinic needles and melts at  $148^{\circ}$ . The tertiary arsine forms crystalline, quaternary iodides with benzyl and *n*- and *iso*-propyl iodides; the benzyl chloride does not crystallise.

[With LUDWIG].—Triphenylarsine, which is conveniently prepared by the action of sodium on an ethereal solution of arsenious chloride and bromobenzene, yields a *platinichloride*,  $AsPh_3 \cdot H_2PtCl_6$ , crystallising in pale yellow leaflets and melting at  $285^{\circ}$ . *Triphenylarsine dichloride*,  $AsPh_3Cl_2$ , produced by passing chlorine into triphenylarsine dissolved in dry carbon tetrachloride, sinters at  $158^{\circ}$  and melts at  $204$ – $205^{\circ}$ ; in the presence of moisture, it readily passes into the more stable *hydroxychloride*,  $AsPh_3Cl \cdot OH$ , a substance melting at  $171^{\circ}$ , which is more directly obtained by passing chlorine into the tertiary base dissolved in commercial chloroform. The hydroxychloride yields a *platinichloride* of exceptional composition,  $(AsPh_3Cl \cdot OH)_3 \cdot PtCl_4$ , which crystallises in yellow needles and melts at  $180$ – $182^{\circ}$ .

*Triphenylarsine dibromide*,  $AsPh_3Br_2$ , separates in white crystals, sinters at  $165^{\circ}$ , and melts at  $215^{\circ}$ .

*Triphenylarsine tetraiodide*,  $AsPh_3I_4$ , formed by mixing its generators in anhydrous solvents, separates from ether in steel-blue needles and melts at  $142$ – $144^{\circ}$ ; the analogous compound,  $AsPh_3Br_2I_2$ , obtained from a mixture of bromine and iodine, crystallises in yellowish-red needles and melts at  $120$ – $121^{\circ}$ .

Triphenylarsine hydroxide (m. p.  $115$ – $116^{\circ}$ ),  $AsPh_3(OH)_2$ , readily obtained from the corresponding chloride or oxychloride by the action of ammonia, is a basic substance yielding the *normal nitrate*,  $AsPh_3(NO_3)_2$ , melting at  $99$ – $100^{\circ}$ , the *basic nitrate*,  $OH \cdot AsPh_3 \cdot NO_3$ , melting at  $160$ – $161^{\circ}$ , and the *basic chromate*,  $AsPh_3(OH) \cdot HCrO_4$ , which is a yellow-red precipitate.

[With K. ULRICH].—Triphenylmethylarsonium iodide combines with chlorine to form a *dichloride*,  $AsPh_3MeICl_2$ , which crystallises from alcohol, acetone, or glacial acetic acid in yellow leaflets and melts at  $144^{\circ}$ ; this additive product is also produced either by the action of hypochlorous acid or the iodide, or by treating the quaternary chloride with iodinechloride. *Triphenylmethylarsonium hydroxide*,  $AsPh_3Me \cdot OH$ , obtained by shaking the iodide with moist silver oxide, crystallises in prisms and melts at  $125$ – $126^{\circ}$ ; it has an alkaline reaction, and when heated at  $100^{\circ}$  decomposes into methyl alcohol and triphenylarsine; the solution rapidly absorbs carbon dioxide, forming the soluble *carbonate*, which separates in large, transparent plates.

[With E. WEISS].—*Triphenylmethylarsonium chloride*, produced either by neutralising the hydroxide with hydrochloric acid, or by digesting the iodide with silver chloride, crystallises in white needles and melts at  $121^{\circ}$ ; the *platinichloride*,  $(AsPh_3Me)_2PtCl_6$ , crystallises in yellowish-red needles melting at  $224$ – $225^{\circ}$ ; the *nitrate*,



separates in long needles and on treatment with a mixture of concen-

trated nitric and sulphuric acids, yields a small amount of *trinitrotri phenylarsonium nitrate*, separating from alcohol as a yellow powder melting at  $195^{\circ}$ ; it is accompanied by a red product, probably an isomeride.

*Triphenylethylarsonium iodide*,  $\text{AsPh}_3\text{EtI}$ , obtained in small yield from its generators at the temperature of the water-bath, crystallises in lustrous needles melting at  $158^{\circ}$ ; the *platinichloride* melts at  $221^{\circ}$ .

*Triphenyliodomethylarsonium iodide*,  $\text{CH}_2\text{I}\cdot\text{AsPh}_3\text{I}$ , produced from methylene iodide and triphenylarsine at  $130^{\circ}$ , crystallises from dilute alcohol in white, silky needles melting at  $227^{\circ}$ , and yields *triphenylchloromethylarsonium iododichloride*,  $\text{CH}_2\text{Cl}\cdot\text{AsPh}_3\cdot\text{ICl}_2$ , separating in yellow crystals melting at  $138^{\circ}$ , and giving rise to triphenylarsonium hydroxide on treatment with sodium hydroxide.

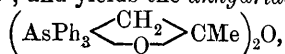
*Triphenyliodomethylarsonium chloride*,  $\text{CH}_2\text{I}\cdot\text{AsPh}_3\text{Cl}$ , crystallises in needles and melts at  $208^{\circ}$ ; *hydroxymethyltriphenylarsonium chloride*,  $\text{OH}\cdot\text{CH}_2\cdot\text{AsPh}_3\text{Cl}$ , obtained by treating the salt,  $\text{CH}_2\text{I}\cdot\text{AsPh}_3\text{I}$ , successively with silver oxide and hydrochloric acid, melts at  $112^{\circ}$ ; the *platinichloride*,  $(\text{OH}\cdot\text{CH}_2\cdot\text{AsPh}_3)_2\text{PtCl}_6$ , melts at  $224^{\circ}$ ; the *iodide* forms yellow, flattened needles and melts at  $171^{\circ}$ .

*Hydroxyethyltriphenylarsonium chloride*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{AsPh}_3\text{Cl}$ , prepared by heating triphenylarsine with ethylene chlorohydrin, crystallises in colourless needles, melts at  $215^{\circ}$ , and gives a *platinichloride* melting at  $223^{\circ}$ .

*Triphenylarsenobetaine hydrochloride*,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{AsPh}_3\text{Cl}$ , produced from triphenylarsine and chloroacetic acid, forms white, soluble needles melting at  $145^{\circ}$ ; the *platinichloride* melts at  $194^{\circ}$ . *Triphenylarsenobetaine*,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{AsPh}_3\cdot\text{OH}$ , set free from the hydrochloride by alcoholic potassium hydroxide, crystallises in soluble, white needles, melts at  $125^{\circ}$ , and yields the *anhydride*,  $\text{AsPh}_3\langle\text{CH}_2\text{O}\rangle\text{CO}$ .

*Triphenylmethylarsenobetaine hydrochloride*,  $\text{COMe}\cdot\text{CH}_2\cdot\text{AsPh}_3\text{Cl}$ , prepared by heating triphenylarsine with chloroacetone, separates in quadratic crystals and melts at  $172^{\circ}$ ; the *platinichloride* is a reddish-brown precipitate.

*Triphenylmethylarsenobetaine*,  $\text{AsPh}_3\langle\text{CH}_2\text{O}\rangle\text{CMe}\cdot\text{OH}$ , produced by treating the preceding salt with alkalis, crystallises in nacreous leaflets, melts at  $123^{\circ}$ , and yields the *anhydride*,



melting at  $194^{\circ}$ .

Triphenylmethylarsenobetaine hydrobromide and hydriodide are soluble in water or alcohol and melt at  $165^{\circ}$  and  $161^{\circ}$  respectively.

*Triphenylphenacylarsonium bromide*,  $\text{AsPh}_3\text{Br}\cdot\text{CH}_2\cdot\text{COPh}$ , obtained from triphenylarsine and bromoacetophenone, crystallises in silky, felted needles and melts at  $178^{\circ}$ ; the *chloride* and *iodide* melt at  $166^{\circ}$  and  $157^{\circ}$  respectively; these salts are soluble in water or alcohol. The *platinichloride* melts at  $191^{\circ}$ ; the *nitrate*, which is insoluble in cold water, dissolves in alcohol, crystallises in needles, and melts at  $184^{\circ}$ .

*Trinitrotriphenylarsine*,  $\text{As}(\text{C}_6\text{H}_4\cdot\text{NO}_2)_3$ , prepared by the action of phosphorous acid on the trinitrotriphenylarsine oxide obtained by

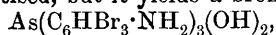


nitrating triphenylarsine, is a yellow, crystalline powder melting at  $250^{\circ}$ .

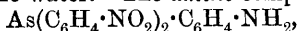
*Trinitrotriphenylarsine dibromide*,  $\text{As}(\text{C}_6\text{H}_4\cdot\text{NO}_2)_3\text{Br}_2$ , and *dichloride* melt at  $204^{\circ}$  and  $228^{\circ}$  respectively.

*Trichlorotrinitrotriphenylarsine oxide*,  $\text{As}(\text{C}_6\text{H}_3\text{Cl}\cdot\text{NO}_2)_3\text{O}$ , produced from the preceding chloride by the action of potassium hydroxide, is a white, crystalline mass melting at  $257^{\circ}$ , yielding the *dibromide*,  $\text{As}(\text{C}_6\text{H}_3\text{Cl}\cdot\text{NO}_2)_3\text{Br}_2$ , melting at  $209^{\circ}$ , and the *arsine*,  $\text{As}(\text{C}_6\text{H}_3\text{Cl}\cdot\text{NO}_2)_3$ , on treatment with phosphorous acid; this base is soluble in the ordinary organic solvents and melts at  $252^{\circ}$ .

Trinitrotriphenylarsine oxide, on reduction, yields the corresponding triamine, the sulphate of which is stable in air, whilst its *tribenzoyl* derivative is a crystalline powder melting at  $271^{\circ}$ . Triaminotriphenylarsine cannot be diazotised, but it yields a bromo-derivative,



with excess of bromine water. The *amino-compound*,



produced by reducing the trinitro-compound with hydrogen sulphide in glacial acetic acid solution, has no basic properties and melts at  $205^{\circ}$ .

*Barium triphenylarsineoxidesulphonate*,  $\text{Ba}_3[\text{AsO}(\text{C}_6\text{H}_4\cdot\text{SO}_3)_3]_2$ , obtained by sulphonating triphenylarsine with concentrated sulphuric acid at  $100^{\circ}$  and treating the product with barium carbonate, is a pale red, soluble, crystalline powder; the free acid was not isolated.

[With F. LAUTERWALD.]—Diphenyl-*p*-tolylarsine,  $\text{AsPh}_2\cdot\text{C}_7\text{H}_7$ , prepared from the interaction of *p*-tolylchloroarsine, bromobenzene, and sodium, is obtained crystalline with considerable difficulty; it melts at  $50^{\circ}$ ; the *mercurichloride*,  $\text{AsPh}_2\cdot\text{C}_7\text{H}_7\cdot\text{HgCl}_2$ , melts at  $147^{\circ}$ , and the *platinichloride*,  $(\text{AsPh}_2\cdot\text{C}_7\text{H}_7)_2\cdot\text{H}_2\text{PtCl}_6$ , at  $233^{\circ}$ .

*Diphenyl-p-tolylarsine hydroxide*,  $\text{C}_7\text{H}_7\cdot\text{AsPh}_2(\text{OH})_2$ , obtained by adding bromine to the arsine and treating the product with hot potassium hydroxide solution, melts at  $68^{\circ}$ ; the *basic nitrate*,  $\text{C}_7\text{H}_7\cdot\text{AsPh}_2(\text{OH})\cdot\text{NO}_3$ , crystallises in yellow needles and melts at  $125^{\circ}$ ; the *sulphide*,  $\text{C}_7\text{H}_7\cdot\text{AsPhS}$ , resulting from the action of hydrogen sulphide on an alcoholic solution of the hydroxide, forms a crystalline, granular mass and melts at  $135^{\circ}$ .

*Diphenyl-p-tolylmethylarsonium iodide*,  $\text{C}_7\text{H}_7\cdot\text{AsPh}_2\text{MeI}$ , formed by the direct union of its generators, separates in druses of white needles and melts at  $152^{\circ}$ ; the *chloride* is oily, the *platinichloride* melts at  $209^{\circ}$ .

*Diphenyl-p-tolyldiethylarsonium iodide*,  $\text{C}_7\text{H}_7\cdot\text{AsPh}_2\text{EtI}$ , is an oil, but the corresponding *platinichloride* separates in red crystals and melts at  $220^{\circ}$ .

*Diphenyloxyarsinobenzoic acid*,  $\text{AsPh}_2\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , obtained by the oxidation of *p*-tolylidiphenylarsine with permanganate, melts at  $253$ — $254^{\circ}$ ; its *silver* and *barium* salts are both soluble.

*Ethyl diphenyldichloroarsinobenzoate*,  $\text{AsPh}_2\text{Cl}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ , produced by saturating an alcoholic solution of the preceding acid with hydrogen chloride, separates on cooling in white crystals melting at  $133^{\circ}$ .

*Diphenylsulphoarsinobenzoic acid*,  $\text{AsPh}_2\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , resulting from the action of hydrogen sulphide on the oxy-acid, melts at  $178^{\circ}$ .

*Phenyldi-p-tolylarsine*,  $\text{AsPh}(\text{C}_7\text{H}_7)_2$ , prepared from phenylchloro-

arsine, bromotoluene, and sodium, crystallises from alcohol in white rhombohedra and melts at  $101^{\circ}$ ; the *mercurichloride*,  $\text{AsPh}(\text{C}_7\text{H}_7)_2\cdot\text{HgCl}_2$ , *platinichloride*, and *dichloride*,  $\text{AsPh}(\text{C}_7\text{H}_7)_2\text{Cl}$ , melts at  $210^{\circ}$ ,  $256^{\circ}$ , and  $194^{\circ}$  respectively. The dichloride, in contact with moisture, gives rise to an *oxychloride*,  $\text{AsPh}(\text{C}_7\text{H}_7)_2\text{OH}\cdot\text{Cl}$ , which melts at  $142\text{--}143^{\circ}$ ; the *oxybromide* is obtained in a similar manner.

*Phenyldi-p-tolylarsine oxide*, obtained by the action of alkalis on the preceding haloid derivatives, is a white powder melting at  $81^{\circ}$ ; it yields a *basic nitrate* crystallising in rosettes of needles and melting at  $94^{\circ}$ , and also a *sulphide*,  $\text{AsPh}(\text{C}_7\text{H}_7)_2\text{S}$ , melting at  $144^{\circ}$ .

*Phenyldi-p-tolylmethylarsonium iodide*,  $\text{AsPh}(\text{C}_7\text{H}_7)_2\text{MeI}$ , crystallises from water in long, white needles, which become yellow on exposure to light and melt at  $84^{\circ}$ ; the *platinichloride* crystallises in yellow needles and melts at  $222^{\circ}$ ; the corresponding *ethiodide*,  $(\text{C}_7\text{H}_7)_2\text{AsPhEtI}$ , melts at  $125^{\circ}$ .

*Phenyloxyarsinodibenzoic acid*,  $\text{AsPhO}(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$ , prepared by oxidising phenyldi-p-tolylarsine with alkaline permanganate solution, is a white, crystalline powder not melting below  $300^{\circ}$ ; its silver and copper salts are insoluble white and blue powders respectively, the latter containing  $1\text{H}_2\text{O}$ ; the *barium* salt is readily soluble. *Diethyl phenyl-dichloroarsinodibenzoate*,  $\text{AsPhCl}_2(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et})_2$ , obtained by saturating an alcoholic solution of the acid with hydrogen chloride, crystallises in aggregates of needles and melts at  $176^{\circ}$ .

*Phenyl-p-tolyloxyarsinobenzoic acid*, also produced by the oxidation of di-p-tolylphenylarsine, does not melt below  $300^{\circ}$ ; its silver salt,  $\text{C}_7\text{H}_7\cdot\text{AsPhO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Ag}$ , crystallises in slender needles; the *dichloro-ester*,  $\text{C}_7\text{H}_7\cdot\text{AsPhCl}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ , is very hygroscopic and melts at  $94^{\circ}$ .

*Tri-p-tolylarsine*, prepared by the general method, separates in triclinic crystals and melts at  $146^{\circ}$ ; the *mercurichloride*, a white, crystalline powder, melts at  $246^{\circ}$ . The *dichloride*,  $\text{As}(\text{C}_7\text{H}_7)_3\text{Cl}_2$ , and the *oxychloride* are crystalline substances, melting respectively at  $228\text{--}230^{\circ}$  and  $185^{\circ}$ ; the *dibromide* melts at  $245^{\circ}$ , and the di-iodide at  $172^{\circ}$ . A *tetraiodide*,  $\text{C}_7\text{H}_7\text{AsI}_4$ , resulting from the action of excess of iodine, forms steel-grey needles melting at  $153^{\circ}$ . The *hydroxide*,  $\text{As}(\text{C}_7\text{H}_7)_3(\text{OH})_2$ , crystallises from alcohol in needles and melts at  $96^{\circ}$ ; the *sulphide*,  $\text{As}(\text{C}_7\text{H}_7)_3\text{S}$ , separates in lustrous leaflets melting at  $170\text{--}171^{\circ}$ .

*Tri-p-tolylmethylarsonium iodide*,  $\text{As}(\text{C}_7\text{H}_7)_3\text{MeI}$ , melts at  $179^{\circ}$ , the *chloride* at  $87^{\circ}$ , the *dichloroiodide*,  $\text{As}(\text{C}_7\text{H}_7)_3\text{MeICl}_2$ , at  $146^{\circ}$ ; the *platinichloride* crystallises from dilute alcohol in reddish-brown, highly refractive prisms.

*Tri-p-tolyliodomethylarsonium iodide*,  $\text{CH}_2\text{I}\cdot\text{As}(\text{C}_7\text{H}_7)_3\text{I}$ , resulting from the direct action of methylene iodide on tri-p-tolylarsine, separates from alcohol in well-defined crystals melting at  $215^{\circ}$ .

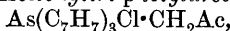
*Tri-p-tolylethylarsonium iodide*,  $\text{As}(\text{C}_7\text{H}_7)_3\text{EtI}$ , crystallises in colourless needles and melts at  $158^{\circ}$ . *Tri-p-tolylallylarsonium bromide*,  $\text{As}(\text{C}_7\text{H}_7)_3\cdot\text{C}_3\text{H}_5\text{I}$ , prepared by heating allyl bromide with the tertiary arsine at  $100^{\circ}$ , crystallises from water in white prisms and melts at

82°; this substance takes up bromine, forming *tri-p-tolyldibromopropylarsonium bromide*,  $\text{As}(\text{C}_7\text{H}_7)_3\text{C}_3\text{H}_5\text{BrI}$ , which melts at 112°.

*Tri-p-tolylallylarsonium iodide* separates in colourless prisms and melts at 141°; the corresponding *chloride* is a yellow oil, yielding a *platini-chloride* which separates as a red powder and melts at 225°.

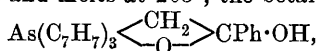
*Tri-p-tolylarsenobetaine hydrochloride*,  $\text{As}(\text{C}_7\text{H}_7)_3\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , obtained as a white, crystalline mass melting at 146°, furnishes a *platini-chloride* melting at 206°; the free betaine is not readily purified.

[With W. KRAHE.]—*Acetonyltri-p-tolylarsonium chloride*,



decomposes at 170°; the free *betaine*,  $\text{As}(\text{C}_7\text{H}_7)_2\left\langle\begin{smallmatrix}\text{CH}_2\\ \text{O}\end{smallmatrix}\right\rangle\text{CMe}\cdot\text{OH}$ , crystallises from dilute alcohol in lustrous needles and melts at 113°; the *platinichloride*,  $[\text{As}(\text{C}_7\text{H}_7)_3\cdot\text{CH}_2\text{Ac}]_2\text{PtCl}_6$ , forms yellow leaflets melting at 210°; the *bromide*,  $\text{As}(\text{C}_7\text{H}_7)_3\text{Br}\cdot\text{CH}_2\text{Ac}$ , melts at 159° and the *iodide* at 144°.

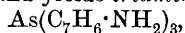
*Tri-p-tolylphenacylarsonium chloride*,  $\text{As}(\text{C}_7\text{H}_7)_3\text{Cl}\cdot\text{CH}_2\cdot\text{COPh}$ , crystallises in white needles melting at 159°; the *platinichloride* forms yellowish-red needles and melts at 205°, the betaine,



separates from alcohol in aggregates of needles and melts at 160°; the *bromide* and *iodide* melt at 182° and 148° respectively.

*Trinitrotri-p-tolylarsine*,  $\text{As}(\text{C}_7\text{H}_6\cdot\text{NO}_2)_3$ , produced by the action of phosphorous acid on trinitrotri-p-tolylarsine oxide (m. p. 212°), the product of the nitration of the tertiary tolylarsine, crystallises in white needles and melts at 201°.

*Trichlorotrinitrotri-p-tolylarsine chloride*,  $\text{As}(\text{C}_6\text{H}_3\text{Cl}\cdot\text{NO}_2)_3\text{Cl}_2$ , which results from the action of dry chlorine on the nitroarsine dissolved in chloroform, melts at 170° and yields *triaminotri-p-tolylarsine*,



on reduction with tin and hydrochloric acid; this base is obtained in white prisms melting at 198°, its *hydrochloride*,  $\text{As}(\text{C}_7\text{H}_6\cdot\text{NH}_2)_3\cdot 3\text{HCl}$ , crystallising in white needles. The *sulphate* is insoluble and the *triacetyl* derivative melts at 228°.

*Triaminotri-p-tolylarsine sulphide*,  $\text{As}(\text{C}_7\text{H}_6\cdot\text{NH}_2)_3\text{S}$ , produced from the triamine and alcoholic ammonium sulphide, is separated from sulphur by alcohol and carbon disulphide; it is insoluble in the organic solvents but dissolves in the dilute mineral acids, sulphuric acid giving rise to the *acid sulphate*,  $2\text{As}(\text{C}_7\text{H}_6\cdot\text{NH}_2)_3\text{S}\cdot 3\text{H}_2\text{SO}_4$ , which is soluble in hydrochloric acid. The *methiodide*,  $\text{As}(\text{C}_7\text{H}_6\cdot\text{NMe}_2)_3\text{MeI}$ , obtained by heating the triaminoarsine with excess of methyl iodide, is a white powder melting indefinitely at 135°.

*Tribenzyltriaminotri-p-tolylarsine*,  $\text{As}(\text{C}_7\text{H}_6\cdot\text{NH}\cdot\text{CH}_2\text{Ph})_3$ , is obtained the form of its hydrochloride by the action of benzyl chloride.

[With HERMANN EISENLOHR.]—*Tri-m-tolylarsine*, prepared from *m*-bromotoluene by the general method, crystallises from alcohol or ether in rhombic, tabular crystals [ $a:b:c = 1.00872:1:1.0355$ ], melts at 96° and has a sp. gr. 1.31 at 18°; the *mercurichloride* melts at 174°, the *hydroxychloride* and *hydroxybromide*, obtained in well-defined crystals, melt at 205° and 190° respectively; the *oxide*, a white, crystalline

mass, melts at  $170^{\circ}$ ; the *sulphide*, which forms silvery needles, melts at  $186^{\circ}$ .

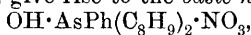
*Tri-m-tolylmethylarsonium iodide*,  $\text{As}(\text{C}_7\text{H}_7)_3\text{MeI}$ , crystallises from water in rhombic prisms and melts at  $181^{\circ}$ ; the *chloride* is oily, the *platinichloride* is a light yellow precipitate, the *ethiodide* separates in modified, triclinic rhombohedra and melts at  $130^{\circ}$ . *Tri-m-tolyl-n-propylarsonium iodide*,  $\text{As}(\text{C}_7\text{H}_7)_3\text{Pr}^{\text{n}}\text{I}$ , slowly formed by the direct combination of the tertiary arsine and propyl iodide at the ordinary temperature, separates in needles and melts at  $143^{\circ}$ ; the *isopropyl* quaternary iodide melts at  $162^{\circ}$ . The interaction of the tertiary arsine and benzyl chloride at  $30\text{--}40^{\circ}$  gives rise to *tri-m-tolylbenzylarsonium chloride*, which melts at  $102^{\circ}$ .

[With M. HEINE.]—*Tri-1:3-xylyl-4-arsine*,  $\text{As}(\text{C}_8\text{H}_9)_3$ , prepared by the general method from 4-bromo-*m*-xylene, crystallises from light petroleum in lustrous, transparent prisms melting at  $166^{\circ}$ ; the *mercurichloride* melts at  $257^{\circ}$ , the *sulphide*, which crystallises in silky prisms, melts at  $145^{\circ}$ . The oxide,  $\text{As}(\text{C}_8\text{H}_9)_3\text{O}$ , formed as a tarry mass by the dehydration of the *hydroxide*,  $\text{As}(\text{C}_8\text{H}_9)_3(\text{OH})_3$ , a substance resulting from the action of alkaline solutions on the dibromide of the tertiary arsine.

*Tri-1:3-xylylmethyl-4-arsonium iodide*,  $\text{As}(\text{C}_8\text{H}_9)_3\text{MeI}$ , melts at  $179^{\circ}$ ; the *chloride* is not crystallisable, but yields a platinichloride separating in reddish-brown crystals melting at  $245^{\circ}$ ; the *ethiodide* could not be obtained.

[With A. SCHAEUBLE.]—*Tri-p-xylylarsine*, prepared from bromo-*p*-xylene and obtained in white prisms melting at  $157^{\circ}$ , yields a *mercurichloride* melting at  $236^{\circ}$ , and a crystalline *chloride*,  $(\text{C}_8\text{H}_9)_3\text{AsCl}_2$ ; its *oxide* is not crystallisable. The *methiodide*, crystallising in plates, melts at  $175^{\circ}$ ; the *platinichloride*, obtained in yellow needles, melts at  $250^{\circ}$ .

[With AD. ROTTER.]—*Phenyldi-1:3-xylylarsine*,  $\text{As}(\text{C}_8\text{H}_9)_2\text{Ph}$ , prepared by the interaction of 4-bromo-*m*-xylenephénylchloroarsine and sodium, crystallises in tabular, triclinic prisms and melts at  $99^{\circ}$ ; the *platinichloride*, separating in yellow, felted needles, decomposes near  $300^{\circ}$ ; the *mercurichloride*, which is obtained in white needles, melts at  $224^{\circ}$ ; the *dichloride* and *oxychloride* melt at  $176^{\circ}$  and  $186^{\circ}$  respectively, whilst the *periodide*,  $\text{As}(\text{C}_8\text{H}_9)_2\text{PhI}_4$ , which forms reddish-violet crystals, melts at  $127^{\circ}$ . The *hydroxide* and *oxide*, which melt respectively at  $112^{\circ}$  and  $120^{\circ}$ , give rise to the *basic nitrate*,



a compound forming transparent crystals and melting at  $126^{\circ}$ . The tertiary arsine forms a *sulphide* and *ethiodide* with great difficulty, the latter compound melting at  $157^{\circ}$ . *Phenyldi-1:3-xylylmethylarsonium iodide*, readily produced from the arsine and methyl iodide, melts at  $184^{\circ}$  and yields the quaternary *hydroxide* melting at  $122^{\circ}$ .

*Trinitrophenyldi-1:3-xylylarsine oxide*,  $\text{AsO}(\text{C}_8\text{H}_8 \cdot \text{NO}_2)_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , obtained by treating the arsine with concentrated nitric and sulphuric acids, separates from alcohol in pale yellow crystals melting at  $245^{\circ}$ .

*Phenyloxyarsinoditolylldicarboxylic acid*,  $\text{AsPhO}(\text{C}_6\text{H}_3 \cdot \text{Me} \cdot \text{CO}_2\text{H})_2$ , and *phenyloxyarsinodiphenyltetra-carboxylic acid*,  $\text{AsPhO}[\text{C}_6\text{H}_3(\text{CO}_2\text{H})_2]_2$ ,

produced by heating the arsine with nitric acid of sp. gr. 1.2 at 110—170°, melt respectively at 196° and 213°.

[With SCHNEEMANN.]—*Tri-p-ethylphenylarsine*,  $\text{As}(\text{C}_6\text{H}_4\text{Et})_3$ , prepared from *p*-bromoethylbenzene by the general method, melts at 78° and yields a *mercurichloride*, *dichloride*, *dibromide*, *hydroxide*, and *sulphide* melting respectively at 132°, 246°, 212°, 180°, and 123°. The *methiodide* and the *trinitro-derivative*,  $\text{AsO}(\text{C}_6\text{H}_3\text{Et}\cdot\text{NO}_2)_3$ , of the corresponding oxide are crystalline and melt at 126° and 232°.

[With D. VON KARCHOWSKI.]—*Tri-ψ-cumylarsine*, prepared in the ordinary way, crystallises in snow-white needles and melts at 223°; its *dibromide* and *hydroxybromide* melt respectively at 224—225° and 108° and give rise to the *hydroxide*,  $\text{As}(\text{C}_9\text{H}_{11})_3(\text{OH})_2$ , which crystallises from dilute alcohol in needles containing  $4\text{H}_2\text{O}$ ; these, on desiccation, over concentrated sulphuric acid yield the pulverulent *oxide* melting at 227—228°.

[With AD. ROTTER.]—*Phenyl-di-ψ-cumylarsine*, prepared from phenylchloroarsine, bromo-ψ-cumene, and sodium, melts at 138.5° and yields the *platinichloride* crystallising in yellow aggregates and melting at 287°; the *aurichloride* forms colourless druses and melts at 177°; the *mercurichloride*,  $\text{AsPh}(\text{C}_9\text{H}_{11})_2\text{HgCl}_2$ , crystallises in needles and melts at 233°; the *dichloride*,  $\text{AsPh}(\text{C}_9\text{H}_{11})_2\text{Cl}_2$ , is a crystalline powder melting at 217°. The *hydroxychloride*, *dibromide*, *di-iodide*, and *hydroxyiodide* melt respectively at 173—175°, 177°, 163.5°, and 153°, and give rise to the *hydroxide*,  $\text{AsPh}(\text{C}_9\text{H}_{11})_2(\text{OH})_2$ , which separates in colourless prisms melting at 113—114°, and yields, on heating or desiccation, the *oxide* melting at 162.5°. The *sulphide*, obtained by heating the tertiary arsine with alcoholic ammonium polysulphide at 110°, melts at 135°. The *methylarsonium iodide*, the *chloride*, and *platinichloride* melt respectively at 179°, 192°, and 266.5°. The quaternary *hydroxide* crystallises in needles softening at 147° and melting at 151°. The *ethylarsonium iodide* melts at 189°.

*Trinitrophenyldi-ψ-cumylarsine oxide*,  $\text{AsO}(\text{C}_9\text{H}_{11}\cdot\text{NO}_2)_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , produced by nitrating the tertiary arsine, melts at 163°.

*Phenyloxyarsinodixylyldicarboxylic acid*,  $\text{AsOPh}(\text{C}_6\text{H}_2\text{Me}_2\cdot\text{CO}_2\text{H})_2$ , *phenyloxyarsinoditolyltetracarboxylic acid*,  $\text{AsOPh}[\text{C}_6\text{H}_2\text{Me}(\text{CO}_2\text{H})_2]_2$ , and *phenyloxyarsinodiphenylhexacarboxylic acid*,  $\text{AsOPh}[\text{C}_6\text{H}_2(\text{CO}_2\text{H})_3]_2$ , result from the action of nitric acid of sp. gr. 1.2 on the tertiary arsine at 110—180°; the first two melt at 199° and 213° respectively, whilst the third yields an anhydride melting at 275°. The *silver* salt of the anhydrotetracarboxylic acid is a white powder; the corresponding *tetraethyl* ester crystallises in silky needles and melts at 193°.

[With W. OBERG.]—*Tri-p-cumylarsine*,  $\text{As}(\text{C}_6\text{H}_4\text{Pr})_3$ , obtained from *p*-bromocumene by the general method, crystallises in colourless prisms melting at 139—140°; the *mercurichloride*,  $\text{As}(\text{C}_9\text{H}_{11})_3\text{HgCl}_2$ , separates in white needles and melts at 243°; the *dichloride* forms white needles, melts at 276°, and yields a *platinichloride*,  $[\text{As}(\text{C}_9\text{H}_{11})_3]_2\text{PtCl}_6$ , crystallising in golden-yellow needles; the *dibromide* melts at 142°; the *oxide*,  $\text{AsO}(\text{C}_9\text{H}_{11})_3$ , and *hydroxy-nitrate*,  $\text{OH}\cdot\text{As}(\text{C}_9\text{H}_{11})_3\cdot\text{NO}_3$ , melt at 129° and 147° respectively.

*Trinitrotricumylarsine oxide*,  $\text{AsO}(\text{C}_6\text{H}_3\text{Pr}\cdot\text{NO}_2)_3$ , produced by nitrating

ing the tertiary arsine, crystallises in pale yellow needles and decomposes at  $245^{\circ}$ .

*Tri-p-cumylarsine sulphide*, prepared by leading hydrogen sulphide into a hot alcoholic solution of the oxide, melts at  $149.5^{\circ}$ .

*Tri-p-cumylmethylarsonium iodide* and the corresponding *ethiodide* melt at  $103^{\circ}$  and  $138^{\circ}$  respectively.

*Trimesitylarsine*,  $\text{As}(\text{C}_6\text{H}_2\text{Me}_3)_2$ , although obtained less readily than the preceding amines, is, nevertheless, produced with less difficulty than the corresponding phosphine; it crystallises from alcohol in prismatic needles and melts at  $170^{\circ}$ ; the *hydroxy-chloride* forms white prisms and melts at  $100^{\circ}$ ; the *dibromide* separates from alcohol in well-defined rhombic prisms and melts at  $237^{\circ}$ ; the *oxide*, produced from the preceding halogen derivatives, melts at  $203-204^{\circ}$ .

*Trimesitylmethylarsonium iodide*,  $\text{As}(\text{C}_9\text{H}_{11})_3\text{MeI}$ , crystallises from alcohol in yellowish-red and from water in white prisms; it melts at  $186^{\circ}$ ; the *chloride* and *platinichloride* melt at  $192^{\circ}$  and  $237^{\circ}$ .

[With A. TRÄGEL].—*Tri-tert.butylphenylarsine*,  $\text{As}(\text{C}_6\text{H}_4\cdot\text{CMe}_3)_3$ , is prepared by heating together bromo-*tert*.butylbenzene and arsenic chloride in a benzene solution; it melts at  $235^{\circ}$  and yields an *oxy-chloride* and *oxide*; the *dichloride* is stable. The *methiodide* decomposes at  $125^{\circ}$ , the quaternary *hydroxide* is obtained in rhombohedral crystals containing  $4\text{H}_2\text{O}$ .

[With H. BÜSCHLER].—*Tri- $\alpha$ -naphthylarsine*,  $\text{As}(\text{C}_{10}\text{H}_7)_3$ , produced from  $\alpha$ -bromonaphthalene, crystallises in slender prisms and melts at  $252^{\circ}$ ; with excess of bromine or chlorine, it gives rise to the *tetra-bromide*,  $(\text{C}_{10}\text{H}_7)_3\text{AsBr}_4$ , or the corresponding *tetrachloride* melting respectively at  $180^{\circ}$  and  $144^{\circ}$ .

The *hydroxy-bromide*, prepared by the action of bromine on a solution of the arsine in a mixture of benzene and alcohol, melts at  $155^{\circ}$  and yields the *hydroxide*,  $\text{As}(\text{C}_{10}\text{H}_7)_3(\text{OH})_2$ , crystallising in needles with  $2\text{H}_2\text{O}$ , and melting above  $300^{\circ}$ .

The *oxide*,  $\text{AsO}(\text{C}_{10}\text{H}_7)_3$ , is obtained by heating the hydroxide at  $110^{\circ}$ ; the sulphide and quaternary iodide could not be obtained.

*Tri- $\beta$ -naphthylarsine*, prepared from  $\beta$ -bromonaphthalene, melts at  $165^{\circ}$  and is purified by the aid of its *mercurichloride*, which crystallises in leaflets and melts at  $247^{\circ}$ . The yield of the naphthylarsines is considerably less than that of the benzenoid derivatives.

*Tri- $\beta$ -naphthylarsine oxide* is readily obtained in the anhydrous condition, the *sulphide*, formed by passing hydrogen sulphide into the alcoholic solution of the resinous *dibromide*, crystallises from this solvent in plates melting at  $162^{\circ}$ .

G. T. M.

## Organic Chemistry.

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**Hydrogenation of Ethylenic Hydrocarbons by the Method of Contact.** By PAUL SABATIER and JEAN BAPTISTE SENDERENS (*Compt. rend.*, 1902, 134, 1127—1130).—When hydrocarbons of the ethylene series up to  $C_8$  are mixed with excess of hydrogen and passed over gently heated reduced nickel, they are converted into hydrocarbons of the methane series. If the temperature is below  $160^\circ$ , the product is practically pure, but above  $200^\circ$  there is partial disruption of the hydrocarbon chain, and paraffins of lower molecular weight are produced together with a small quantity of condensed products.

Reduced copper behaves similarly, but must be heated more strongly. It does not produce the hydrogenation of hydrocarbons which do not contain at least one unsubstituted  $CH_2$  group. Styrene is converted into ethylbenzene. Limonene, at about  $190^\circ$ , is converted into a hydrocarbon,  $C_{10}H_{18}$ , which boils at  $170^\circ$  (corr.), and has a sp. gr. 0.827 at  $0^\circ/0^\circ$ . In presence of nickel, the limonene is converted into hexahydrocymene, and is therefore an isomeride of menthene (compare *Abstr.*, 1901, i, 195).  
C. H. B.

**Acid Nature of Acetylene.** By JEAN BILLITZER (*Zeit. physikal. Chem.*, 1902, 40, 535—544).—The solubility of acetylene is increased by the addition of barium or ammonium hydroxide and diminished by the addition of potassium or sodium hydroxide, sodium sulphate, or sulphuric acid, the lowering being greatest for the sodium sulphate and least for the acid. The solubility of ethylene is similarly affected, but although the effect of the sodium sulphate is almost identical in the two cases, yet the alkalis produce a much greater decrease of solubility of ethylene than of acetylene. The author considers that this indicates an acid character of acetylene and the consequent formation of small quantities of salts. From the results, the dissociation of acetylene is estimated as about one-tenth of that of water, hence it follows that the reaction between calcium carbide and water must, at atmospheric pressure, be almost complete, or about 99.99 per cent.

L. M. J.

**Trimethylenecarbinol and its Derivatives.** By PAUL DALLE (*Bull. Acad. Roy. Belg.*, 1902, 36—79).—When trimethylenecarbonylonitrile (*Abstr.*, 1899, i, 676) is reduced by sodium in alcohol, it furnishes the corresponding *amine*, a colourless liquid soluble in water, alcohol, or ether; this boils at  $86^\circ$  under 758 mm. pressure, and has a sp. gr. 0.8114 at  $16^\circ$ ,  $n_D$  1.4251 at  $19^\circ$ , and  $K$  0.044. It is precipitated from its aqueous solution by potassium carbonate or hydroxide. The *hydrochloride* is white and hygroscopic, soluble in water or alcohol; the *platinichloride* forms golden-yellow lamellæ, slightly soluble in cold water. The hydrochloride, by treatment with sodium nitrite, furnishes *trimethylenecarbinol*,  

$$\begin{array}{c} CH_2 \\ | \\ CH_2 > CH \cdot CH_2 \cdot OH, \end{array}$$
 a colourless, slightly aromatic liquid, which boils

at 125—126° under 756 mm. pressure, has a sp. gr. 0.9122 at 16°,  $n_D$  1.43041, and is soluble in all ordinary solvents, but is precipitated from its aqueous solutions by addition of potassium carbonate or hydroxide. With hydrochloric acid, *trimethylenecarbinyll chloride*,  $\begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix} > \text{CH} \cdot \text{CH}_2\text{Cl}$ , is formed, a colourless, pleasant smelling liquid which boils at 85—86° under 756 mm. pressure, and has a sp. gr. 0.9647 at 16°. The corresponding *bromide* boils at 109—110° under 750 mm. pressure, and has a sp. gr. 1.387 at 16°; it does not combine with bromine, but with hydrogen bromide at 170° forms tetramethylene dibromide. The *iodide* is formed by the action of sodium iodide at 100° on either of the foregoing compounds dissolved in methyl alcohol. It is a colourless liquid, but becomes brown on exposure to air, boils at 135° under 760 mm. pressure, has a sp. gr. 1.725 at 16°, and is insoluble in water, but soluble in alcohol or ether. The *acetate* is a colourless liquid having an odour like that of ethyl acetate; it boils at 134° under 758 mm. pressure, has a sp. gr. 0.9605 at 16°, and is soluble in alcohol or ether but insoluble in water. The *isobutyrate* has similar properties, boils at 164° under 763 mm. pressure, has a sp. gr. 0.9378 at 16°, and is insoluble in water. The *trimethylenecarboxylate* is a slightly odorous, colourless liquid which boils at 191° and has a sp. gr. 0.9972 at 16°. Trimethylenecarboxylic acid,  $\begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix} > \text{CH} \cdot \text{CO}_2\text{H}$ , produced by alkaline hydrolysis of the corresponding nitrile, has  $K$  0.00144; with phosphorus trichloride, it furnishes the *chloride*, a colourless, mobile liquid which boils at 119° under 760 mm. pressure, has a sp. gr. 1.185 at 17°; with ammonia, this is converted into the *amide*, which crystallises from ether, melts at 120°, and dissolves in alcohol but is insoluble in water. The *isobutyl ester* boils at 173—174° under 761 mm. pressure, and has a sp. gr. 0.9208 at 16°.

Methyltrimethylene derivatives in general have lower boiling points than the corresponding tetramethylene compounds, but the difference is not constant in value; compared with *isobutyl* compounds, the former have higher densities and conversely smaller mol. volumes, whilst the difference in boiling points of corresponding compounds is about 17° for mono-substituted derivatives such as *isobutyl chloride* (68.5°), and trimethylenecarbinyll chloride (85—86°), and about 24° to 28° for tri-substituted compounds such as the corresponding nitriles.

T. A. H.

**Formation of  $\alpha$ -Decylglycol from *iso*Valeraldehyde.** By HUGO ROSINGER (*Annalen*, 1902, 322, 131—133).—The results already published by the author (*Abstr.*, 1901, i, 669) completely contradict Nef's conclusions as to the formation of  $\alpha$ -decylglycol from valeraldehyde and powdered sodium hydroxide (this vol., i, 7); the substance produced is, in reality, the mono*iso*valerate of this glycol.

G. T. M.

**Phosphomannitic Acid and Phosphomannitates.** By L. PORTES and G. PRUNIER (*J. Pharm. Chim.*, 1902, [vi], 15, 457—466).—By heating mannitol and phosphoric acid together for several days



in molecular proportion, *phosphomannitic acid* is formed. When purified, it is a gummy, colourless, very hygroscopic mass, and is dibasic, yielding both acid and normal salts. The *barium* salt, which forms a white, crystalline powder, is readily soluble in cold water, is partially decomposed by boiling water, and is insoluble in alcohol, ether, essential or fatty oils. Its solutions do not give the reaction of phosphoric acid with ammonium molybdate. The phosphomannitates of magnesium, iron, calcium, potassium, and sodium have also been prepared; with the exception of the magnesium salt, they are all amorphous.

A. F.

**Ether Explosions.** By E. VON NEANDER (*Chem. Zeit.*, 1902, 26, 336—337).—The residue obtained on evaporating the ethereal solution of a fat occasionally explodes violently during drying. It is found that when it has been kept for some months ether contains a quantity of active oxygen (estimated by the oxidation of hydriodic acid), equivalent to 0.24 per cent. of hydrogen peroxide. The active oxygen is possibly present in the form of ethyl peroxide,  $(C_2H_5)_4O_3$  (Berthelot). On evaporation of such ether, a residue is obtained which does not explode; the presence of a fat is necessary. When an ethereal solution of a fat containing 0.14 per cent. of active oxygen was evaporated, the residue did not explode, but a vapour with a characteristic, unpleasant odour was given off. The evolution of this vapour was always noticed in those cases when an explosion occurred.

K. J. P. O.

**Action of Phosphorus Chlorides on Organic Acids. Preparation of Trichloroacetyl Chloride.** By MAURICE DELACRE (*Bull. Acad. roy. Belg.*, 1902, 189—202).—The action of phosphorus trichloride on organic acids has been represented by the following equations: (a)  $3X \cdot CO_2H + 2PCl_3 = 3X \cdot COCl + P_2O_3 + 3HCl$  (Gal, *Rep. Chim. pur.*, 1863, 5, 36); (b)  $3X \cdot CO_2H + PCl_3 = 3X \cdot COCl + P(OH)_3$  (Wilde, *Bull. Acad. roy. Belg.*, 16, 487); (c)  $6X \cdot CO_2H + 3PCl_3 = 6X \cdot COCl + 3HPO_2 + 3HCl$  (Bechamp, *Compt. rend.*, 1885, 40, 944; 41, 23).

The author finds, as has already been observed by Thorpe (*Trans.*, 1880, 37, 186) in the case of acetyl chloride, that the preparation of trichloroacetyl chloride is best represented by equation (a), and points out that the latter also holds for the preparation of isobutyryl chloride (Burcker, *Ann. Chim. Phys.*, 1882, [v], 26, 468) and trimethylacetyl chloride (Tissier, *ibid.*, 1893, [vi], 29, 384), whence he concludes that it is generally applicable to this reaction; moreover, equation (c) is not in accordance with the amount of hydrogen chloride produced in practice, whilst equation (b) would seem to imply that the constitution of phosphorous acid is as written below, and that the two atoms of hydrogen in water do not possess the same function.  $3H \cdot HO + PCl_3 = P(HO)_3 + 3HCl$ .

T. A. H.

**Attempt to Resolve Monochlorosulphoacetic Acid [into Optical Isomerides].** By CH. PORCHER (*Bull. Soc. Chim.*, 1902, [iii], 27, 438—441).—The author has succeeded in resolving mono-

chlorosulphoacetic acid into its optical isomerides by means of the cinchonine salt, although as yet he has not obtained them in a pure condition. The work is being continued. A. F.

**Reactivity of Alkyloxy-acids.** By REINHOLD VON WALTHER (*J. pr. Chem.*, 1902, [ii], 65, 479—480).—Sodium methoxide and ethoxide react with ethyl chloroacetate in alcoholic solution; at the ordinary temperature, a crystalline, sodium compound is formed, but at 150° sodium chloride is eliminated and a product obtained which is probably a mixture of ethyl alkyloxyacetate, dialkyloxy-acetoacetate, and alkyloxychloroacetoacetate. With chloroacetamide, sodium ethoxide and 2-methoxyphenoxy (guaiacyloxy) react in a similar fashion; in these cases, satisfactory yields of ethoxy- and of 2-methoxyphenoxy-acetamide are obtained, melting at 80° and 138° respectively.

These alkyloxy-esters, and yet more the aryloxy-esters, readily undergo condensation with other substances. Ethyl phenoxyacetate condenses with benzyl cyanide to form phenoxyacetylbenzyl cyanide, melting at 125°, and with acetophenone to form  $\gamma$ -benzoyl- $\alpha$ -phenoxyacetone,  $\text{OPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CPhO}$ , which will undergo further condensations, even with anthranilic acid. C. F. B.

**Oxidised Oils.** By JULIUS LEWKOWITSCH (*Analyst*, 1902, 27, 139—145).—The results obtained in the examination of commercial blown Ravison rape oil, East India rape oil, and cotton-seed oil, solid linseed oil, and blown maize oil are tabulated. The oxidised acids contained in these oils were separated and investigated. They all showed considerably higher saponification values than acid values. That they are not saturated acids is shown by the comparatively high iodine numbers. The presence of lactones is indicated by the differences between the saponification and acid values, and lactic compounds were actually separated from the oxidised acids. The other fatty acids, which had been freed from oxidised acids, also contained small quantities of lactones. The oxidised acids were soluble in water to a considerable extent. W. P. S.

**The Origin and Nature of the Free Acid formed during Hübl's Reaction with Unsaturated Compounds.** By HERBERT INGLE (*J. Soc. Chem. Ind.*, 1902, 21, 587—595).—The formation of the free acid produced during the action of iodine chloride solutions on unsaturated compounds is due to the action of water on the iodo-chlorides, and the quantity of the free acid is dependent on the structure of the compound and the amount of the water present. The nature of this acid was found to vary with the structure of the unsaturated compound. In using Wijs' reagent, the solution became dark brown in colour, probably due to the action of free hydriodic acid on iodine chloride, hydrogen chloride and iodine being formed. Some iodochlorides are reduced by potassium iodide, free iodine being liberated, causing a reduction in the apparent iodine absorption. This error may, in part, be avoided by the addition of more chloroform to dissolve the iodochlorides formed, and also by adding water to the test

solution before potassium iodide. Iodine chloride is stated to be the active substance in "addition" and not hypiodous acid. Some doubly linked carbon atoms, by the protecting influence of neighbouring groups, may be prevented from absorbing any halogen from a strongly acid Hübl's solution (Waller's), so that by determining the iodine value of a substance by Waller's, Wijs', and Hübl's methods, and the free acid formed during the latter reaction, the number of doubly linked atoms and their relative position in the molecule may be ascertained. In the methods ordinarily employed, substitution does not take place.

W. P. S.

**Glycerides of Fatty Acids with double Melting Point.** By HANS KREIS (*Chem. Zeit.*, 1902, 26, 384—385).—The author finds that the glycerides obtained by fractional crystallisation from ether of beef, mutton, and pork fat exhibit the phenomena of a double melting point, that is, they melt at a given temperature to a clear liquid, which at a higher temperature becomes turbid, and finally again clear. Hansen (*Chem. Zeit.*, 1902, 26, 93) only observed a single melting point for these glycerides.

K. J. P. O.

**Halogen-substituted Malonic Acids and their Derivatives.** By MAX CONRAD and H. REINBACH (*Ber.*, 1902, 35, 1813—1821. Compare Willstätter, this vol., i, 342).—Chloromalonic acid can be quantitatively prepared by the action of the calculated quantity of sulphuryl chloride on malonic acid in solution in dry ether; the *lead* salt is a white precipitate, the *aniline* salt is crystalline and melts with evolution of carbon dioxide at 118°. Dichloromalonic acid was prepared in a similar manner by means of sulphuryl chloride; the *aniline* salt is crystalline and melts at 105° with evolution of carbon dioxide. Bromomalonic acid can easily be prepared by the action of bromine on an aqueous solution of sodium malonate or on an ethereal solution of malonic acid; the acid melts with evolution of carbon dioxide at 113° (compare Petrieff, this Journal, 1874, 787, and *Abstr.*, 1878, 490); the *lead* salt is a white, crystalline precipitate; the *potassium* salt crystallises in slender needles. Dibromomalonic acid is very easily prepared by slowly adding bromine to malonic acid covered with aqueous hydrochloric or hydrobromic acid (compare Petrieff, *loc. cit.*, and Willstätter, *loc. cit.*); it melts and evolves carbon dioxide at 147°. The *lead* salt crystallises in long, slender needles which explode on heating; the *potassium* salt forms small needles, the *silver* salt is a white, crystalline precipitate. The *aniline* salt is crystalline, melts and evolves carbon dioxide at 113°, and in aqueous solution quickly becomes converted into aniline dibromoacetate.

Dibromomalonic acid can be nearly quantitatively converted into mesoxalic acid when it is heated with concentrated aqueous sodium hydroxide at 100°; sodium mesoxalate crystallises out on cooling. When sodium mesoxalate is treated with aniline in the presence of acetic or hydrochloric acid, the *aniline* salt of dianilinomalonic acid is formed; it melts and evolves carbon dioxide at 120°, and on boiling with water is converted into aniline and mesoxalic acid. In the preparation of methyl dianilinomalonate (this vol., i, 210), the addition

of potassium acetate is recommended, as in the presence of this salt the methyl dibromomalonate is converted into methyl mesoxalate, which then reacts with aniline.

*Methyl benzylbromomalonate* is obtained when methyl benzylmalonate is brominated in ethereal solution, and crystallises in white prisms melting at  $56^{\circ}$ ; on hydrolysis with sodium hydroxide, benzyltartronic acid (m. p.  $147^{\circ}$ ) is obtained.

Methyl chlorobromomalonate crystallises in prisms melting at  $37^{\circ}$ .

K. J. P. O.

**Monoethyl  $\alpha$ -Anilinopyrotartarate Mononitrile [ $\beta$ -Anilino- $\beta$ -cyanobutyrate] and its Products of Transformation.** By GEORG SCHROETER and CARL KIENBERGER (*Ber.*, 1902, 35, 2078—2080).—Ethyl  $\beta$ -anilino- $\beta$ -cyanobutyrate, prepared by Schiller-Wechsler's method (*Abstr.*, 1885, 900) by the action of aniline on the cyanohydrin obtained from ethyl acetoacetate, was hydrolysed with sulphuric acid; the amide,  $\text{NHPh}\cdot\text{CMe}(\text{CO}\cdot\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , thus obtained melted at  $109^{\circ}$  (Schiller-Wechsler gave  $125^{\circ}$ ) and is readily converted, with elimination of alcohol, into  $\alpha$ -anilino- $\alpha$ -methylsuccinimide, which melts at  $167^{\circ}$  (Schiller-Wechsler,  $150^{\circ}$ ), forms a crystalline hydrochloride, and is identical with the substance prepared by Strauss (*Abstr.*, 1892, 1195) by the action of prussic acid on ethyl  $\beta$ -anilinoacrylate and subsequent treatment of the product with sulphuric acid. Attention is drawn to the fact that if this nitrile is treated with sulphuric acid without taking precautions as regards temperature, &c., a mixture of amide and imide is obtained, a fact which probably accounts for the conflicting results of previous authors.

K. J. P. O.

**New Dimethylglutaric Acid.** By EDMOND E. BLAISE (*Compt. rend.*, 1902, 134, 1113—1115. Compare *Abstr.*, this vol., i, 357).—In the action of phosphorus pentabromide on ethyl hydroxypivalate (*loc. cit.*), besides ethyl bromopivalate, an oily liquid is formed; the latter, when hydrolysed by potassium hydroxide, yields a *phosphate* of hydroxypivalic acid,  $\text{OH}\cdot\text{PO}(\text{O}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H})_2\cdot\text{H}_2\text{O}$ ; it forms crystals losing  $\text{H}_2\text{O}$  at  $100^{\circ}$  and melting at  $147^{\circ}$ , behaves as a tribasic acid, forms a series of well-crystallised salts, and is very resistant to hydrolysis.

Ethyl bromopivalate condenses with ethyl potassicocyanacetate with the production of an *ester*,  $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$ , which boils at  $166^{\circ}$  under 16 mm. pressure. When this ester is hydrolysed and the substituted malonic acid thus obtained decomposed by heat, an acid is produced which can be purified in the form of its *anhydride*. The latter is a liquid boiling at  $165$ — $167^{\circ}$  under 34 mm. pressure; with aniline, it yields an *anilide* melting at  $131^{\circ}$ , which, on heating, loses water, forming a *phenylimide* melting at  $189^{\circ}$ ; with *p*-toluidine, a *p*-toluidide is formed melting at  $138^{\circ}$ . When the anhydride is boiled with water, an *acid*,  $\text{C}_7\text{H}_{12}\text{O}_4$ , is obtained, which melts at  $74$ — $75^{\circ}$  and is not oxidised by heating with a mixture of nitric and sulphuric acids. From its method of formation, this acid should be  $\alpha$ -dimethylglutaric acid and identical with the acid obtained by the

oxidation of camphor. This, however, is not the case. It is suggested that, possibly, in the preparation of the acid here described, a profound intramolecular change has taken place, and that the acid is an  $\alpha\beta$ -dimethylglutaric acid. K. J. P. O.

**Oxidation of Glucosone to Trihydroxybutyric Acid.** By ROBERT S. MORRELL (*Proc. Camb. Phil. Soc.*, 1902, 11, 340—341).—Glucosone (*Trans.*, 1899, 75, 345; 1900, 77, 1219), when oxidised with bromine, gives trihydroxybutyric acid, which was identified in the form of the calcium salt. The calcium salt is very soluble in water and the solution gives, with lead acetate, a precipitate which is insoluble in dilute acetic acid.

Calcium trihydroxybutyrate is reduced by hydriodic acid and phosphorus, giving butyric acid. J. McC.

**Diethyl  $\beta$ -Anilino-tricarballic Acid Mononitrile and its Products of Transformation.** By GEORG SCHROETER and CARL KIRNBERGER (*Ber.*, 1902, 35, 2081—2084. Compare preceding page).—Ethyl anilacetonedicarboxylate combines with hydrogen cyanide forming a *cyanohydrin*,  $\text{NHPh}\cdot\text{C}(\text{CN})(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ , which forms crystals melting at  $29^\circ$ . When cautiously treated with concentrated sulphuric acid, the corresponding *amide* is obtained, to

which is assigned the formula 
$$\begin{array}{c} \text{NHPh}\cdot\text{C}(\text{CH}_2\cdot\text{CO}_2\text{Et})\cdot\text{CO} \\ | \\ \text{CH}_2-\text{C}(\text{OH})(\text{OEt}) \end{array} > \text{NH};$$
 it

forms crystals melting at  $126^\circ$ . If the cyanohydrin or the amide is treated with concentrated sulphuric acid for some time, an *imide* is formed with elimination of alcohol,

$$\begin{array}{c} \text{NHPh}\cdot\text{C}(\text{CH}_2\cdot\text{CO}_2\text{Et})\cdot\text{CO} \\ | \\ \text{CH}_2-\text{CO} \end{array} > \text{NH};$$

this substance is a crystalline powder melting at  $167^\circ$  and has an acid reaction; its *acetyl* derivative melts at  $178^\circ$ . On treatment with ethyl iodide and sodium in alcoholic solution, an *ethyl* derivative is

obtained, 
$$\begin{array}{c} \text{NHPh}\cdot\text{C}(\text{CH}_2\cdot\text{CO}_2\text{Et})\cdot\text{CO} \\ | \\ \text{CH}_2-\text{CO} \end{array} > \text{NEt},$$
 forming large crystals melting

at  $68^\circ$ , and is no longer soluble in alkalis. By the action of sodium on alcoholic solutions of the amide or imide, a *disodium* salt is

formed, 
$$\begin{array}{c} \text{NHPh}\cdot\text{C}(\text{CH}_2\cdot\text{CO}_2\text{Na})\cdot\text{CO} \\ | \\ \text{CH}_2-\text{CO} \end{array} > \text{NNa},$$
 which is very hygro-

scopic; on acidification of an aqueous solution, the corresponding *acid* is obtained; the latter begins to decompose at  $57^\circ$  and is only completely melted at  $100^\circ$ ; the double *silver* salt, with silver nitrate,  $\text{C}_{12}\text{H}_{11}\text{O}_4\text{N}_2\text{Ag}_2\cdot\text{AgNO}_3$ , is a white precipitate. K. J. P. O.

**Dimethyl Hydrogen Citrate.** By GEORG SCHROETER and LEONHARD SCHMITZ (*Ber.*, 1902, 35, 2085—2088. Compare preceding abstract).—*Dimethyl hydrogen citrate*,  $\text{C}_8\text{H}_4(\text{OH})(\text{CO}_2\text{Me})_2\cdot\text{CO}_2\text{H}\cdot\text{H}_2\text{O}$ , can be prepared by one hour's boiling of a solution of citric acid in methyl alcohol containing a very small quantity of sulphuric acid; the ester is isolated as calcium salt; it crystallises in prisms or needles (from water), which melt, but not sharply, at  $125$ — $126^\circ$ , and on heating decompose with loss of water and methyl alcohol, possibly forming an

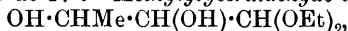
internal anhydride. The *calcium* salt is a white powder; the *silver* salt crystallises in leaflets; the *copper* salt forms blue crystals with  $1\text{H}_2\text{O}$ .

K. J. P. O.

**Synthesis of Aldehydes.** By LOUIS BOUVEAULT and ANDRÉ WAHL (*Compt. rend.*, 1902, 134, 1145—1147).—When nitroisobutylene is reduced by aluminium amalgam or by zinc powder and acetic acid, it yields *isobutaldoxime*, the corresponding hydroxylamine probably being formed as an intermediate product. Under similar conditions, nitrostyrene yields phenylacetaldoxime.

C. H. B.

**The Acetal of Crotonaldehyde and its Conversion into Methyltriase.** By ALFRED WOHL and FRANZ FRANK (*Ber.*, 1902, 35, 1904—1910).— $\beta$ -*Chlorobutyralacetal*,  $\text{CHMeCl}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$ , prepared by the action of alcoholic hydrogen chloride on crotonaldehyde, boils at  $70\text{--}71^\circ$  under 12 mm. pressure and has a sp. gr. 0.975 at  $17^\circ$ . *Crotonacetal*,  $\text{CHMe}\cdot\text{CH}\cdot\text{CH}(\text{OEt})_2$ , prepared by distilling the preceding compound from potassium hydroxide, boils at  $146\text{--}148^\circ$ , and has a sp. gr. 0.8475 at  $17^\circ$ . *Methylglyceraldehyde acetal*,



prepared by the action of 6 per cent. permanganate on the preceding compound, is a colourless, odourless, viscous liquid of bitter, burning taste, boils at  $110\text{--}120^\circ$  under 12 mm. pressure, and has a sp. gr. 1.0498 at  $17^\circ$ ; unlike the two preceding compounds, which are insoluble, it is miscible with water in all proportions. *Methylglyceraldehyde*,  $\text{OH}\cdot\text{CHMe}\cdot\text{CH}(\text{OH})\cdot\text{CHO}$ , prepared by the action of cold sulphuric acid on the acetal, is isolated by neutralising with baryta and evaporating the solution in a vacuum at  $25\text{--}30^\circ$ ; it was obtained as a colourless syrup, of sweet, somewhat bitter taste, miscible with water and alcohol; for combustion, it was mixed with sand and dried over phosphoric oxide. The *phenylosazone*,  $\text{C}_{16}\text{H}_{18}\text{ON}_4$ , separates from hot benzene as a yellow, crystalline powder, sinters at  $171^\circ$ , melts at  $171.5^\circ$  (corr.), and decomposes at  $190^\circ$ . The *phenylbenzylhydrazone*,  $\text{C}_{17}\text{H}_{20}\text{O}_2\text{N}_2$ , is a colourless compound which crystallises from ether and melts at  $116^\circ$ .

*$\beta$ -Hydroxybutyralacetal*,  $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$ , is a colourless, mobile liquid, boils at  $79\text{--}81^\circ$  under 12 mm., and at  $190\text{--}195^\circ$  under 760 mm. pressure, dissolves in five parts of water, and cannot be oxidised to the corresponding ketone.

T. M. L.

**Derivatives of Milk Sugar.** By RUD. DITMAR (*Ber.*, 1902, 35, 1951—1953).—Hepta-acetylchlorolactose, obtained by Bodart's method, melts, when recrystallised from ether, at a lower temperature ( $116\text{--}129^\circ$ ) than when precipitated from benzene by light petroleum; in the latter case, the crystals melt at  $126\text{--}141^\circ$ . When the acetyl compound is boiled in methyl alcoholic solution with silver carbonate, *hepta-acetylmethyl-lactoside*,  $\text{C}_{12}\text{H}_{14}\text{O}_4(\text{OAc})_7\text{Me}$ , is obtained; it is precipitated from benzene solution by adding light petroleum as a crystalline mass, melts at  $65\text{--}66^\circ$ , reduces Fehling's solution, and is hydrolysed by an excess of baryta to lactose. By carefully boiling, however, with only a slight excess of the alkali, a *methyl-lactoside*,  $\text{C}_{12}\text{H}_{21}\text{O}_{11}\text{Me}$ , is obtained which melts at  $171^\circ$ .

*Hepta-acetylbromolactose*,  $C_{26}H_{35}O_{17}Br$ , is obtained by agitating carefully dried lactose with acetyl bromide for 8 hours in a flask from which moisture and light are excluded; it crystallises from ether in long prisms, melts at  $138^{\circ}$ , and has  $[\alpha]_D + 108.17$  at  $14^{\circ}$  in chloroform; for bright blue light, it has  $[\alpha] + 130.87$  at  $14^{\circ}$ . W. A. D.

**The Initiative Action of Iodine and of other Oxidisers in the Hydrolysis of Starch and Dextrins.** By F. E. HALE (*Amer. J. Sci.*, 1902, [iv], 13, 379—399).—In titrations with iodine, using starch as indicator, a reddish colour is often observed in place of the usual blue; in the titration, too, there is frequently a loss of iodine. If an absolutely pure and fresh starch solution be employed, no red colour is developed and there is no loss of iodine. Ordinary starch, however, contains two impurities, one of which gives a red colour with iodine, and the other, by the action of oxygen and potassium hydrogen carbonate, is transformed into that one which becomes red with iodine. The latter of the two (which is coloured blue with iodine) appears to be identical with the amidulin produced by the digestion of pure starch by saliva, whilst the former is erythroextrin, which is the second salivary digestion product. The loss of iodine is attributed to the formation of erythroextrin from the amidulin, the iodine acting in an oxidising capacity. That the loss of iodine is due to the starch is proved by the fact that hydrogen peroxide or potassium permanganate in presence of potassium hydrogen carbonate can oxidise starch so that starch iodide is not formed on the addition of iodine.

Experiments have been made with starch solutions prepared in different ways, and the loss of iodine with ordinary impure starch is quite apparent. The suggestion made by Girard (*Abstr.*, 1887, 868) that potato starch absorbs three times as much iodine as rice starch has not been confirmed.

Attempts were made to isolate the impurities of starch, but these were not successful. It has, however, been shown that the compound which is coloured red by iodine can be produced by treatment of pure starch in potassium hydrogen carbonate solution with hydrogen peroxide or potassium permanganate. The impurity which is coloured blue with iodine, gives an iodide which is not precipitated by sulphuric acid, and differs, therefore, from starch iodide. The presence of erythroextrin was recognised polarimetrically. The author discusses the mechanism of the hydrolysis by iodine. J. McC.

**Conversion of Lactim Ethers into Lactams.** By WILHELM WISLICENUS and HEINRICH KÖRBER (*Ber.*, 1902, 35, 1991—1992. Compare *Abstr.*, 1900, i, 435; this vol., i, 211).—An almost theoretical yield of tetramethyluric acid is obtained when methoxycaine is heated at  $200^{\circ}$  for three hours. When ethoxycaine is heated at  $240^{\circ}$  for four hours, the product is 1:3:7-trimethyl-9-ethyl-2:6:8-tri-oxypurine melting at  $197$ — $198^{\circ}$ . J. J. S.

**New Method for the Preparation of Nitriles.** By HANS BUCHERER (*Chem. Centr.*, 1902, i, 911; from *Zeit. Farben. Textilchem.*, 1902, 1, 70—72).—Nitriles may be prepared by the action of potass-

ium cyanide on the additive compounds of Schiff's bases with sodium hydrogen sulphite. The latter compounds may be used in solution as prepared if an excess of the sulphite is avoided. A concentrated solution of potassium cyanide is added, and the mixture heated on the water-bath. The nitrile quickly separates in the form of an oil.

E. W. W.

**Methylindenes from Coal Tar.** By JOHANNES BOES (*Ber.*, 1902, 35, 1762—1764).—The coal tar fraction boiling at 200—210°, when freed from phenols and bases, is further purified by means of the picrate, and the hydrocarbon mixture thus obtained is fractionated and gives on analysis numbers corresponding with the formula  $C_{10}H_{10}$ . When boiled for some time with dilute nitric acid, the product yields a mixture of trimellitic and hemimellitic acids which are separated by means of their barium salts. Each of these tricarboxylic acids corresponds with two methylindenes, and in all probability the four possible isomerides are present in the mixture under examination.

G. T. M.

**Triphenylmethane and Concentrated Sulphuric Acid.** By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1902, 35, 1754. Compare this vol., i, 381).—Triphenylmethane, when prepared by Friedel and Crafts' method, always contains traces of anthracene which are not readily removed by recrystallisation. It is to the presence of this impurity that the development of a yellow coloration with concentrated sulphuric acid is due, pure triphenylmethane dissolving to a colourless solution.

G. T. M.

**Triphenylmethane.** By FRITZ ULLMANN (*Ber.*, 1902, 35, 1811—1813. Compare preceding abstract).—Baeyer and Villiger (this vol., i, 380) have stated that triphenylmethane dissolves unchanged in sulphuric acid with a yellow coloration. The author finds that triphenylmethane is not dissolved by sulphuric acid, but only by fuming sulphuric acid, and then without any marked coloration; in the latter case, sulphonic acids are formed. When triphenylmethane is left for a long time under sulphuric acid, or when the hydrocarbon is heated with it at 80°, the sulphuric acid becomes yellow, but very little substance is dissolved. Further, if triphenylmethane containing a trace of triphenylchloromethane or triphenylcarbinol is shaken with sulphuric acid, the latter immediately becomes intensely yellow.

K. J. P. O.

**Triphenylmethyl. IV.** By MOSES GOMBERG (*Ber.*, 1902, 35, 1822—1840. Compare *Abstr.*, 1901, i, 77, 319, 638, 690).—Triphenylmethyl is best prepared by treating a solution of triphenylmethyl chloride in benzene with zinc; the solution immediately becomes yellow, and an additive compound of zinc chloride and triphenylmethyl chloride separates as an oil; after 5—15 days, the benzene is completely evaporated and the residue boiled with acetone; triphenylmethyl remains as a white, crystalline mass, which soon becomes yellow; in the dry state, it is fairly stable; its solutions are all yellow, and rapidly oxidise in the air, triphenylmethyl peroxide



separating. Triphenylmethyl forms an *additive* compound with 1 mol.  $C_6H_6$ , which is obtained as large, colourless crystals when acetone is added to a solution of the hydrocarbon in benzene; it loses benzene when heated at  $80-90^\circ$ .

Triphenylmethyl immediately absorbs iodine, becoming converted into triphenylmethyl iodide; the additive compounds with ethyl acetate or benzene behave in a similar manner. On titrating the hydrocarbon with iodine in an organic solvent, it was found that only from  $80-85$  per cent. of the theoretical amount of iodine combined with the triphenylmethyl; some triphenylmethyl peroxide was always formed at the same time. From the solution of triphenylmethyl iodide thus obtained, triphenylmethylamine (m. p.  $103^\circ$ ) was prepared by the action of ammonia. In a similar manner, *triphenylmethylethylamine* and *triphenylmethylpropylamine* were prepared; the former melted at  $75-77^\circ$ , the latter at  $70-72^\circ$ . *Triphenylmethylamine*, similarly obtained, is an oil which on boiling with dilute acids is converted into triphenylcarbinol; from the triphenylmethyl iodide, triphenylmethylaniline (m. p.  $149-150^\circ$ ), triphenylmethyl-*o*-toluidine, and triphenylmethyl-*p*-toluidine were also prepared.

Triphenylmethyl bromide and iodide form pentabromo- and penta-iodo-additive compounds when the constituents are mixed in chloroform, benzene, or carbon disulphide solution.

*Triphenylbromomethane pentabromide* forms red crystals which lose bromine in the air; the *pentaiodide* forms well-defined crystals melting at  $92^\circ$ . *Triphenyliodomethane pentaiodide* crystallises in small prisms, melting at  $90^\circ$ , and is more stable than triphenylmethyl iodide (see below). By water, these perhaloids are converted into triphenylcarbinol, but by alcohol into triphenylmethane; in the presence of zinc dust or finely divided silver, alcohol converts them into triphenylmethyl ethyl ether. With acetyl chloride, the last mentioned substance does not yield triphenylmethyl acetate (Allen and K  lliker, Abstr., 1885, 655) but triphenylmethyl chloride. The author finds that triphenylmethyl acetate, prepared from triphenylmethyl chloride and silver acetate, melts at  $87-88^\circ$ .

In solution in ethyl acetate, the perhaloids are converted by zinc dust into triphenylmethyl.

*Triphenylmethyl iodide* can be prepared by mixing solutions of triphenylmethyl and iodine in warm petroleum, and forms large yellow crystals, which rapidly become brown with separation of iodine; it melts at  $132^\circ$ . When its solutions are exposed to the air, decomposition rapidly takes place, triphenylcarbinol, triphenylmethyl peroxide, and iodine being formed. Silver chloride converts triphenylmethyl bromide and iodide into triphenylmethyl chloride.

Most phenylhalogenmethanes readily form well crystallised additive compounds with metallic chlorides when the solutions of the constituents in ether benzene, ethyl acetate, &c., are mixed. By this means, a red, crystalline *additive* compound from antimony pentachloride and trichloromethyl chloride has been obtained. Tritolylmethyl chloride yields an orange *additive* compound with zinc chloride, a yellow crystalline *compound* with ferric chloride, and a red *compound* with

mercuric chloride. Similar substances have been prepared from benzotrichloride, benzophenone chloride, and diphenylmethyl bromide.  
K. J. P. O.

**Basic Properties of Carbon.** By PAUL WALDEN (*Ber.*, 1902, 35 2018—2031).—In order to investigate the basic nature of carbon in triphenylmethane derivatives, the electrical conductivities have been determined of solutions in sulphur dioxide of the following compounds: triphenylcarbinol, trimethylcarbinol, triphenylmethyl chloride and bromide, methyl iodide, allyl iodide, benzyl bromide, ethyl iodoacetate, *isobutyl* phenylbromoacetate,  $\omega$ -bromostyrene, iodobenzene,  $\alpha$ -bromonaphthalene, *tert.*butyl iodide, dipentene dihydrobromide, and dipentene dihydriodide.

For triphenylcarbinol,  $\Delta$  was found to be 4.04, for  $v$  85.59, and 6.23 for  $v$  260, where  $\Delta$  is expressed in reciprocal ohms, and  $v$  is the volume in litres containing one gram-mol. The solution in sulphur dioxide was pale yellow, and deposited yellow leaflets melting and decomposing at 152°. On evaporation of the solvent, colourless triphenylcarbinol was obtained melting at 158—159°. The conductivity of this substance is comparable to that of tertiary bases, quinoline, pyridine, &c., and of dimethylpyrone. Trimethylcarbinol gave  $\Delta$  0.0066 for  $v$  20.5; the solution was colourless. The conductivity of triphenylcarbinol is therefore not due to the basic character of the oxygen. For triphenylmethyl chloride  $\Delta$  was 8.34, for  $v$  34.3, and 22.97 for  $v$  284; monomethylammonium chloride gave  $\Delta$  10.15 for  $v$  32, and  $\Delta$  22.76 for  $v$  266; the former behaves as a true binary salt. The complex salt of triphenylmethyl chloride and stannic chloride,  $\text{CPh}_3\text{SnCl}_5$ , gave an intensely yellow solution with a conductivity comparable with that of potassium iodide:

	$v$ .	$\Delta$ .	$v$ .	$\Delta$ .
$\text{CPh}_3\text{SnCl}_5$ .....	113	60.82	518	87.16
KI .....	128	61.7	512	92.7

Triphenylmethyl bromide formed an intensely yellow solution, the conductivity of which shows it to be one of the best electrolytes; thus for  $v$  295,  $\Delta = 126.4$ . Trimethylsulphonium chloride, and tetramethylammonium chloride and bromide have similar conductivities.

Of the other primary, secondary, and tertiary bromides and iodides investigated, only *tert.*butyl iodide,  $\text{CMe}_3\text{I}$ , gave a yellow solution in sulphur dioxide with a measurable conductivity; for  $v$  112.5,  $\Delta = 0.99$ , and for  $v$  266,  $\Delta = 1.41$ .

As dipentene and pinene show certain similarities with triphenylmethyl, both absorbing oxygen from the air and combining directly with water, it is suggested that these terpenes contain tervalent carbon; the conductivity of dipentene dihydriodide is also in agreement with this hypothesis; thus for  $v$  121.4,  $\Delta = 12.6$ , and for  $v$  327.1,  $\Delta = 16.5$ .

Attention is drawn to the fact that accompanying the change of acid character into basic character in the case of compounds of sulphur, oxygen, iodine, and nitrogen, there is a raising of valency; thus the acid

bivalent sulphur of hydrogen sulphide becomes the basic quadrivalent sulphur of the sulphonium bases. From this point of view, acid characters should be associated with bivalent carbon. K. J. P. O.

**Action of Arylamines on Benzene-*m*-sulphonic Chloride and Toluene-2:4-disulphonic Chloride.** By JULIUS TROEGER and W. MEINE (*Ber.*, 1902, 35, 1959—1960).—*Toluene-2:4-disulphonanilide*,  $C_6H_3Me(SO_2 \cdot NPh)_2$ , separates from dilute alcohol in white crystals and melts at  $189^\circ$ . The *o*-toluidide forms pale violet crystals and melts at  $170$ — $171^\circ$ . The *m*-toluidide melts at  $138^\circ$ . T. M. L.

**Action of Phenylcarbimide on the Esters of some Oxy-acids.** By EUGÈNE LAMBLING (*Bull. Soc. Chim.*, 1902, [iii], 27, 441—451).—In the present communication, the author gives a number of supplementary details with regard to the properties of some of the compounds previously described (*Abstr.*, 1899, i, 52). The phenylurethane of glycollic acid,  $NPh \cdot CO \cdot O \cdot CH_2 \cdot CO_2H$ , when purified by crystallisation from chloroform, melts at  $141^\circ$ , passing at the same time into the internal anhydride. When boiled with an aqueous solution of sodium hydroxide, it decomposes with formation of carbonic and glycollic acids and aniline. The *sodium* salt, with  $2H_2O$ , crystallises in slender needles; the *ammonium* salt forms slender, anhydrous needles; the *barium* salt, which crystallises with  $3H_2O$ , is obtained as a felted mass of microscopic prisms; the *silver* salt forms slender needles. The lactam derived from the phenylurethane of glycollic acid crystallises in microscopic needles melting at  $126^\circ$ , is very sparingly soluble in cold water, and when boiled with it undergoes partial retransformation into the acid; it is also soluble in hot alcohol or benzene and in chloroform, but insoluble in ether. When heated with a solution of sodium carbonate, it passes into solution as the corresponding sodium salt. It has no basic properties. The author has also determined approximately the condition of equilibrium between the acid, anhydride, and water at the boiling point in the case of a 0.6 per cent. solution.

The phenylurethane of lactic acid melts at  $142^\circ$  and undergoes decomposition into aniline, carbon dioxide, and lactic acid when heated with water in a sealed tube at  $150$ — $160^\circ$ . The *barium* and the *silver* salts crystallise in microscopic prisms. The lactam derived from the above acid melts at  $142^\circ$ .

The *sodium* salt of the phenylurethane of phenylglycollic acid crystallises, with  $3H_2O$ , in slender needles very soluble in hot water; the *barium* salt, which also contains  $3H_2O$ , is obtained by double decomposition as a mass of microscopic needles, and the *silver* salt forms a mass of anhydrous, slender needles. A. F.

**Thiocyanates and *iso*Thiocyanates [Thiocarbimides].** By HENRY L. WHEELER and HENRY F. MERRIAM (*J. Amer. Chem. Soc.*, 1902, 24, 439—448. Compare *Abstr.*, 1901, i, 514; this vol., i, 28, 366).—A mixture of methylene thiocyanate and thiobenzoic acid in benzene solution, when heated on the water-bath, deposits yellow crystals of *methylene dithiocarbamate*,  $CH_2(CS \cdot S \cdot NH_2)_2$ , which melts at  $166^\circ$ , and from the solution *methylene thiobenzoate benzoyldithiocarb-*

*amate*,  $\text{COPh}\cdot\text{NH}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{S}\cdot\text{COPh}$ , was isolated in the form of yellow prisms which melt at  $138-139^\circ$ . *Methylene benzoyldithiocarbamate*,  $\text{CH}_2(\text{S}\cdot\text{CS}\cdot\text{NH}\cdot\text{COPh})_2$ , was also produced as yellow crystals melting at  $130-131^\circ$ , and hydrogen cyanide and carbon disulphide are simultaneously produced in the reaction.

*Methylene thiobenzoate*,  $\text{CH}_2(\text{S}\cdot\text{COPh})_2$ , prepared by treating potassium thiobenzoate with methylene iodide, was obtained in the form of white needles, melting at  $120^\circ$ , which are insoluble in alkali.

A mixture of ethylene thiocyanate and thiobenzoic acid gives *ethylene dithiocarbamate* melting at  $188-189^\circ$ , and *benzoylimino-*

*methylene ethylene disulphide*,  $\begin{array}{c} \text{CH}_2\cdot\text{S} \\ | \\ \text{CH}_2\cdot\text{S} \end{array} > \text{C:N}\cdot\text{COPh}$ , which crystallises in colourless, prismatic tablets melting at  $80-81^\circ$ ; the constitution of the latter was proved by preparing it from thiocynoethylsulphine hydrochloride and benzoyl chloride. It is insoluble in aqueous alkali but is decomposed by alcoholic potassium hydroxide.

Chloroethylene thiocyanate and thiobenzoic acid in benzene solution, when heated on the water-bath, give a white deposit of *iminomethylene ethylene disulphide hydrochloride*, which can be crystallised from alcohol or ether in thin plates which blacken at  $200^\circ$  and melt at  $212^\circ$ . In the same way, styrene thiocyanate gives crystals of *benzoylimino-*

*methylene phenylethylene disulphide*,  $\begin{array}{c} \text{CHPh}\cdot\text{S} \\ | \\ \text{CH}-\text{S} \end{array} > \text{C:Nbz}$ , which melts at  $135^\circ$ . Trimethylene thiocyanate gives with thiobenzoic acid *trimethylene benzoyldithiocarbamate*,  $\text{CH}_2(\text{CH}_2\cdot\text{S}\cdot\text{CS}\cdot\text{NHBz})_2$ .

Trimethylene thiocyanate, when heated on the water-bath with aniline and then precipitated with ether, gives tabular or prismatic crystals of *phenyl- $\psi$ -trimethylenedithiobiuret*,  $\text{CH}_2 < \begin{array}{c} \text{CH}_2\cdot\text{S}\cdot\text{C}(\text{NH}) \\ \text{CH}_2\cdot\text{S}\cdot\text{C}(\text{NH}) \end{array} > \text{NPh}$ , which melts at  $173^\circ$ . In the same way, styrene thiocyanate gives  *$\psi$ -phenylethylenephenyldithiobiuret*, which crystallises from a mixture of alcohol and ether in colourless plates melting at  $205^\circ$ .

*m-Xylene thiocyanate* is formed from *m-xylene* and potassium thiocyanate; it separates from alcohol in colourless crystals melting at  $160-161^\circ$ . With benzylidene chloride, potassium thiocyanate gives a mixture of benzaldehyde and ethyl thiocyanate. Methyl dibromohydrocinnamate, when treated with potassium thiocyanate, loses a mol. of bromine, and  *$\psi$ -cyanogen disulphide* and an unsaturated compound (methyl cinnamate) are formed. The same reaction takes place with other 2 : 3-dibromo-compounds. J. McC.

**Conversion of Arylhydroxylamines into Diarylcarbamides.** Arylmethylenehydroxylamines. By EUGEN BAMBERGER and HENRY DESTRAZ (*Ber.*, 1902, 35, 1874—1885).—Hydroxydiphenylformamidine,  $\text{NPh}\cdot\text{CH}\cdot\text{NPh}\cdot\text{OH}$ , when treated with acetic anhydride at the atmospheric temperature, is converted into *s-diphenylcarbamide*, which in turn is partially converted into the acetyl derivative; the method by which the isomeric change takes place was not determined.

*Copper di-p-tolxyloxyformamidine*,  $\text{Cu}[\text{O}\cdot\text{N}(\text{C}_7\text{H}_7)\cdot\text{CH}\cdot\text{N}\cdot\text{C}_7\text{H}_7]_2$ , pre-

pared by the action of anhydrous copper sulphate and sodium acetate on alcoholic di-*p*-tolylmethylenedihydroxylamine, separates from xylene in glistening prisms and melts at 263·5°.

*Di-p-tolxyloxyformamidine hydrochloride*,  $C_{15}H_{17}ON_2Cl$ , separates as a white powder on adding hydrochloric acid to the copper salt suspended in hot acetone, and is precipitated from aqueous solution by concentrated hydrochloric acid in white, pearly needles melting at 198—199°. Acetic anhydride converts it into di-*p*-tolylcarbamide and its acetyl derivative. *Acetyl-di-p-tolylcarbamide* crystallises from benzene in glistening, white needles, melts at 140°, and is hydrolysed by alcoholic potash into di-*p*-tolylcarbamide.

The copper salt of *di-p-chlorophenylxyloxyformamidine*,  
 $C_6H_4Cl \cdot N(OH) \cdot CH \cdot N \cdot C_6H_4Cl$ ,  
 prepared from dichlorophenylmethylenedihydroxylamine, crystallises from xylene in short, brown, felted needles. When heated with acetic anhydride, it is converted into di-*p*-chlorophenylcarbamide and its acetyl derivative, the latter melting at about 160°.

Di-1 : 4 : 2-xylenemethylenedihydroxylamine,  
 $CH_2[N(OH) \cdot C_6H_3Me_2]_2$   
 (Abstr., 1900, i, 341), is reduced by aluminium amalgam to *p*-xylidine, and methyl-*p*-xylidine,  $C_6H_4Me_2 \cdot NHMe$ . Anhydrous copper sulphate converts it into the copper salt of *di-p-xylyloxyformamidine*,  $C_6H_3Me_2 \cdot N \cdot CH \cdot N(OH) \cdot C_6H_3Me_2$ , which is a reddish-brown powder and does not melt at 300°; considerable quantities of azoxy-*p* xylene are also produced.

*N-Glyoxime-p-xylyl ether*,  $C_6H_3Me_2 \cdot N \left\langle \begin{array}{c} CH \cdot CH \\ | \quad | \\ O \quad O \end{array} \right\rangle N \cdot C_6H_3Me_2$ , is produced, together with *p*-xylidine and *p*-azoxyxylene, by heating di-*p*-xylylmethylenedihydroxylamine on a water-bath; it crystallises from alcohol or benzene in sulphur-yellow, silky, felted needles, melts at 204—205°, and by phenylhydrazine in acetic acid solution is converted into glyoxalosazone.

*Di-1 : 3 : 4-xylylmethylenedihydroxylamine*,  $CH_2[N(OH) \cdot C_6H_3Me_2]_2$ , from *as-m*-xylylhydroxylamine and formaldehyde, crystallises from benzene or from a mixture of chloroform and light petroleum in white, heavy crystals and melts at 128—129°; like other *o*-substituted methylene-ethers, it gives no colour with ferric chloride or copper acetate; it is decomposed by heat into *m*-xylyl-*N*-glyoxime, and by copper sulphate into dixyloxyformamidine.

*Di-o-tolylmethylenedihydroxylamine*,  $CH_2[N(OH) \cdot C_6H_4Me]_2$ , separates from alcohol as a snow-white, crystalline powder, melts at 116—116·5°, and gives no coloration with ferric chloride or copper acetate; acetic anhydride converts it into glyoxime-*N*-phenyl ether or oxanilide (a product of the further action of acetic anhydride on the glyoxime ether), together with acetanilide, azoxybenzene, and *acetyl-phenylhydroxylamine*,  $C_6H_5 \cdot NAc \cdot OH$ , which separates from light petroleum in glistening, flat needles, melts at 67—67·5°, and differs from formylphenylhydroxylamine mainly in that it does not form a sparingly soluble copper salt.

Formylphenylhydroxylamine,  $C_6H_5 \cdot N(OH) \cdot CHO$  (this vol., i, 279),

is best prepared from phenylhydroxylamine and anhydrous formic acid, and by cautiously heating with phosphoric oxide is converted into phenylcarbimide.

T. M. L.

**Etherification of Pyrogallol.** By WILHELM HIRSCHER (*Monatsh.*, 1902, 23, 181—198. Compare *Monatsh.*, 1889, 10, 150).—When treated with potassium hydroxide and ethyl bromide, pyrogallol yields chiefly the triethyl ether, accompanied by an oil from which ethylcatechol diethyl ether, ethylpyrogallol triethyl ether, and a substance boiling at 149—150° under 15 mm. pressure, apparently isomeric with the latter, have been isolated.

*Ethylcatechol diethyl ether* boils at 121° under 15 mm. pressure. When boiled with hydriodic acid, it is hydrolysed to *ethylcatechol*, a mobile, colourless liquid, soluble in alcohol, insoluble in water, which distils unchanged under reduced pressure, does not solidify at -10°, becomes brown on exposure to air, gives with ferric chloride a dirty green colour changing through intense violet to ruby-red on addition of sodium carbonate, forms a voluminous precipitate with lead acetate, and reduces ammoniacal silver nitrate in the cold. When boiled with acetic anhydride and sodium acetate, it forms a white *acetyl* derivative melting at 53°. With fuming nitric acid, it yields *dinitroethylcatechol diethyl ether* crystallising from alcohol in long, greenish needles which melt at 83°. The alcoholic mother liquor yields a derivative of lower melting point, probably the *mononitro*-compound. The action of bromine on ethylcatechol diethyl ether in glacial acetic acid solution and of nitric acid on the oil so formed leads to the formation of *bromonitroethylcatechol diethyl ether*, which crystallises in long needles, melts at 78°, and with fuming nitric acid yields *bromodinitroethylcatechol diethyl ether* melting at 65—66°.

*Ethylpyrogallol triethyl ether* boils at 143° under 15 mm. pressure, and with fuming nitric acid yields *dinitroethylpyrogallol triethyl ether*, which crystallises from alcohol in colourless needles, melts at 51°, and becomes dark yellow on exposure to light. The alcoholic mother liquor yields a substance which melts at 45°, and is probably the *mononitro*-derivative. The action of sulphuric acid on pyrogallol triethyl ether leads to the formation of the *sulphonic acid* which crystallises from water in nodules. An attempt to liberate the sulphonic acid from its lead salt by means of sulphuric acid resulted in hydrolysis to pyrogallol triethyl ether. When treated with an excess of bromine in acetic acid solution, the triethyl ether yields *tribromopyrogallol triethyl ether*, which melts at 38—39°. *Bromopyrogallol diethyl ether*, formed by warming pyrogallol triethyl ether with 1 mol. of bromine in acetic acid solution, crystallises in needles and melts at 103—104°. On addition of 1 mol. of bromine to the triethyl ether in cold acetic acid solution and addition of water, an oil is formed which is converted by nitric acid into *bromonitropyrogallol triethyl ether*, crystallising from alcohol in thin needles and melting at 104°. As this bromonitro-derivative is also obtained by bromination of Schiffer's nitropyrogallol triethyl ether (*Abstr.*, 1892, 715), it must have the constitution  $[(\text{OEt})_3 : \text{Br} : \text{NO}_2 = 1 : 2 : 3 : 4 : 5]$ . With fuming nitric acid, it yields *bromodinitropyrogallol triethyl ether*, which melts at 74°.

G. Y.

**Hexahydro-*o*-toluic Acid.** By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1902, 26, 335).—*Hexahydro-*o*-toluic acid* [2-methylcyclohexanecarboxylic acid], obtained when *o*-toluic acid is reduced by means of amyl alcohol and sodium, melts at 50° and boils at 242°; the *anilide* melts at 148°. At the same time, a second isomeric acid is formed, identical with that obtained by Perkin and Goodwin (*Trans.*, 1895, 67, 119); the latter boils at 236–237° and forms an *anilide* melting at 66°.

K. J. P. O.

**Nitration with Ethyl Nitrate.** By WILHELM WISLICENUS and ANTON ENDRES (*Ber.*, 1902, 35, 1755–1762).—Ethyl nitrate, in the presence of sodium or sodium ethoxide, condenses with compounds containing a reactive methylene group to yield *isonitro*-derivatives,  $CXY:NO_2Na$ .

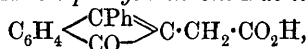
*Ethyl sodium isonitrophenylacetate*,  $CPh:(NO_2Na)CO_2Et$ , prepared by condensing ethyl phenylacetate and ethyl nitrate with sodium suspended in dry ether, was not obtained in a state of purity. Its existence was demonstrated by hydrolysing the crude product with concentrated sodium hydroxide solution when the sodium derivative of *isonitrophenylmethane* was produced. The new compound resembles nitrophenylmethane in forming a labile *iso*-modification. This is shown by acidifying the aqueous solution of its sodium salt, extracting with ether, and adding ferric chloride; a brownish-red coloration is developed, which disappears slowly after a time, and very rapidly on warming. The property of developing the coloration is recovered by reconvertng the substance into its metallic derivative and repeating the preceding experiment.

*isoNitrobenzyl cyanide*, obtained by the condensation of benzyl cyanide and ethyl nitrate in the presence of sodium or sodium ethoxide suspended in dry ether, is isolated in the form of its *sodium* derivative,  $CN \cdot CPh:NO_2Na$ , a compound separating from alcohol as a brown, crystalline mass; it gives a deep green coloration with ferric chloride, and with silver nitrate yields the *silver* derivative,  $CN \cdot CPh:NO_2Ag$ , a pale yellow, crystalline powder decomposing energetically on heating. When freshly liberated from a solution of its sodium derivative, the nitro-compound probably has the *isonitro*-configuration, for it develops a red coloration with ferric chloride; it is, however, very unstable and rapidly changes into a resinous product. The nitro-compound, when distilled in steam, yields a small amount of stilbene dicyanide, and on reduction with zinc dust and sodium hydroxide gives rise to *isonitroso*-benzyl cyanide, the yield being 70 per cent. of the theoretical; hydrolysis with concentrated alkali hydroxide solution leads to the production of sodium *isonitrophenylmethane*, and affords a ready means of preparing this substance.

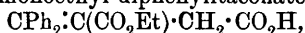
The action of alcoholic hydrogen chloride on the nitro-compound results in the formation of stilbene dicyanide and nitrous acid; the presence of ethyl nitrophenylacetate was not indicated. An attempt to prepare a methyl derivative from sodium *isonitrobenzyl cyanide* with methyl iodide at 100° led to the production of *isonitrosobenzyl cyanide*.

G. T. M.

**Indoneacetic Acids. I. 3-Phenyl-1-indone-2-acetic Acid and 3-Phenyl-1-hydrindone-2-acetolactone.** By HANS STOBBE and WALTHER VIEWIG (*Ber.*, 1902, **35**, 1727—1737).—The principal product of the action of cold concentrated sulphuric acid at 10° on  $\gamma$ -diphenylitaconic acid is 3-phenyl-1-indone-2-acetic acid,



which crystallises from benzene in small, lustrous, orange-yellow prisms and melts at 167·5°; the *barium* salt,  $(\text{C}_{17}\text{H}_{11}\text{O}_3)_2\text{Ba} \cdot 3\text{H}_2\text{O}$ , forms orange-red needles, the *calcium* salt is reddish-yellow, and the *silver* salt yellow and sensitive to light. The *semicarbazone*,  $\text{C}_{18}\text{H}_{15}\text{O}_3\text{N}_3$ , crystallises from alcohol in yellow needles and melts and decomposes at 218—220°. The *ethyl* ester,  $\text{C}_{19}\text{H}_{16}\text{O}_3$ , of the acid, obtained by adding diethyl diphenylitaconate dissolved in light petroleum to concentrated sulphuric acid is dimorphous; it crystallises from light petroleum in dull, triclinic prisms melting at 81·5°, and from alcohol and benzene in silky, rhombic plates melting at 77°; when melted, the triclinic form is converted into the rhombic one. The same ethyl ester is obtained, along with the phenylindoneacetic acid, by the action of sulphuric acid on monoethyl diphenylitaconate,



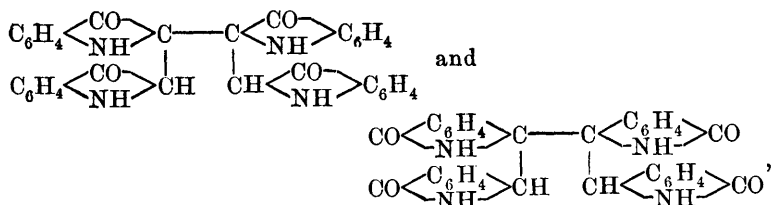
a result which can only be explained by assuming that the alcohol originally eliminated in forming the indoneacetic acid esterifies the latter. That an indone acid, and not a naphthalene derivative, is formed by the action of sulphuric acid on  $\gamma$ -diphenylitaconic acid, is held to be proved from the following considerations: (1) the yellow colour of the products—a phenylketodihydronaphthoic acid would be colourless; (2) oxidation of the acid with alkaline potassium permanganate gives *o*-benzoylbenzoic acid; (3) with bromine, two isomeric, colourless *monobromolactones*,  $\text{C}_{17}\text{H}_{11}\text{O}_3\text{Br}$ , are obtained; an  $\alpha$ -ketodihydronaphthoic acid would give a stable dibromide; (4) concentrated mineral acids convert the indoneacetic acid into an isomeric saturated *lactone*, the identity of this compound with the lactone next described is uncertain.

3-Phenyl-1-hydrindoneacetolactone,  $\text{C}_6\text{H}_4 \cdot \text{CPh} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{CH} \cdot \text{CH}_2$ , obtained as a

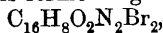
bye-product of the action of concentrated sulphuric acid on  $\gamma$ -diphenylitaconic acid, separates from carbon disulphide in white, triclinic crystals, melts at 119—120°, and is converted by bases into the isomeric phenylindoneacetic acid; the *semicarbazone*,  $\text{C}_{18}\text{H}_{15}\text{O}_3\text{N}_3$ , crystallises from alcohol in colourless, woolly needles and melts and decomposes at 256—261°. W. A. D.

**Indigotin and Indigo-red.** By WILHELM VAUBEL (*Chem. Centr.*, 1902, i, 936; from *Zeit. Farben. Textilchem.*, 1902, 1, 39—45. Compare *Abstr.*, 1901, i, 714).—When indigotin and indigo-red are reduced intermediate products,





are formed respectively. These compounds differ from the colourless end-products in forming red solutions when dissolved in alcoholic solutions of alkalis; the reduction product of indigo-red has a deeper colour than indigo-red itself. Attempts to prepare optically active indigo-white failed. By the action of potassium bromide and potassium bromate on indigotin suspended in sulphuric acid or dissolved in chloroform, *m*-bromoisatin is formed together with a compound,



which melts at 125° and is soluble in ether or chloroform.

E. W. W.

**Isomeric *cis-trans*- $\alpha$ -Keto- and  $\alpha$ -Hydroxy-lactones and Selection in the Formation of Compounds with Several Asymmetric Carbon Atoms.** By EMIL ERLENMEYER, jun. (*Ber.*, 1902, 35, 1935—1943. Compare Erlenmeyer and Lux, *Abstr.*, 1898, i, 668).—Similar results are obtained on reducing  $\alpha$ -oxy- $\beta$ -phenyl- $\gamma$ -benzylbutyrolactone and  $\alpha$ -oxy- $\gamma$ -phenyl- $\beta$ -benzylidenebutylolactone as were given formerly by  $\alpha$ -oxy- $\beta$ - $\gamma$ -diphenylbutyrolactone (*loc. cit.*).

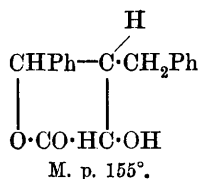
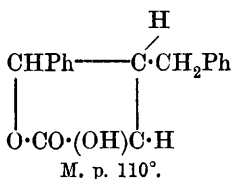
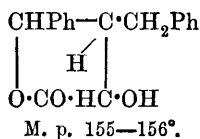
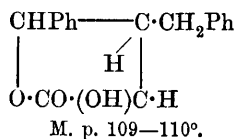
$\alpha$ -Oxy- $\beta$ -phenyl- $\gamma$ -benzylbutyrolactone,  $\text{CH}_2\text{Ph} \cdot \text{CH} \begin{array}{c} \diagup \text{CHPh} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CO}$ , when reduced with sodium amalgam, gives a mixture of two stereoisomeric *hydroxy-lactones*,  $\begin{array}{c} \text{CHPh} \\ | \\ \text{H} \cdot \text{C}(\text{OH}) \cdot \text{CO} \cdot \text{O} \\ | \\ \text{CHPh} \cdot \text{CH} \cdot \text{CH}_2\text{Ph} \\ | \\ \text{OH} \cdot \text{CH} \cdot \text{CO} \cdot \text{O} \end{array}$  and

the former is the more soluble in chloroform, crystallises in needles, and melts at 113°, the latter separating in prisms and melting at 153°. These substances are accompanied by an *acid*,  $\text{C}_{17}\text{H}_{16}\text{O}_3$ , melting at 161°, which, by boiling mineral acids, is converted into an isomeric *acid* melting at 128°.

$\alpha$ -Oxy- $\gamma$ -phenyl- $\beta$ -benzylidenebutylolactone,  $\text{CHPh} \cdot \text{C} \begin{array}{c} \diagup \text{CHPh} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{CO} \cdot \text{O}$ , on reduction with zinc dust and acetic acid, gives two racemic *stereoisomerides*, which can be denoted by the formulæ  $\text{CH}_2\text{Ph} \cdot \text{CH} \begin{array}{c} \diagup \text{CHPh} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{CO} \cdot \text{O}$

and  $\text{H} \cdot \text{C}(\text{CH}_2\text{Ph}) \begin{array}{c} \diagup \text{CHPh} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{CO} \cdot \text{O}$ ; the one more soluble in water melts at 134°, the other melting at 137°; the latter alone is obtained on condensing benzylpyruvic acid with benzaldehyde. Along with the stereoisomerides, an *acid*,  $\text{C}_{17}\text{H}_{16}\text{O}_3$ , melting at 143° is obtained, which, by boiling with mineral acids, is converted into an isomeric *acid* melting at 97°.

Each of the stereoisomeric keto-lactones gives two racemic hydroxy-lactones when reduced by sodium amalgam; the two forms obtained from the keto-lactone melting at 134° melt at 109—110° and 155—156°, and those from the lactone melting at 137° at 110° and 155°; the four forms seem to be distinct, and can be represented by the formulæ:



Starting with the racemic form (+ -) of an unsaturated compound containing one asymmetric carbon atom, reduction has given rise to the two racemic forms  $\begin{pmatrix} + & - \\ - & + \end{pmatrix}$  and  $\begin{pmatrix} + & - \\ + & - \end{pmatrix}$ , corresponding with a derivative containing two asymmetric carbon atoms; the four hydroxy-lactones, which contain three such asymmetric carbon atoms, correspond with the racemic forms:



W. A. D.

**Nitrated Phenylglutaric Acids and their Reduction Products.** By GEORG SCHROETER and HANS MEERWEIN (*Ber.*, 1902, 35, 2073—2078).—On nitrating  $\beta$ -phenylglutaric acid, a mixture of *o*- and *p*-nitro-derivatives is obtained; these are separated by extracting the mixture with boiling water, in which only the ortho-derivative is soluble.  $\beta$ -*p*-Nitrophenylglutaric acid crystallises in needles melting at 240°; its methyl ether melts at 65°. The *o*-nitro-acid crystallises in pale yellow leaflets melting at 174°; its methyl ester forms white needles melting at 41°.  $\beta$ -2:4-Dinitrophenylglutaric acid, prepared by nitrating the *p*-nitro-acid, crystallises in long, yellow needles melting at 177°; its methyl ester forms large crystals melting at 50°.  $\beta$ -*p*-Aminophenylglutaric acid, obtained by reducing the corresponding nitro-derivative with ammonium sulphide or alcoholic stannous chloride, crystallises in needles melting and decomposing at 217°; the methyl ester forms white leaflets melting at 63°; the copper salt, with 2H<sub>2</sub>O, forms a pale green powder, the acetyl derivative leaflets melting at 103°.

On reducing *o*-nitrophenylglutaric acid with ammonium sulphide, an acid was formed which crystallised and melted at 204·5°, its methyl

ester crystallised in prisms melting at  $65.5^{\circ}$ ; with alcoholic stannous chloride, on the other hand, *hydrocarbostyryl-4-acetic acid*,  $C_6H_4 \begin{matrix} \text{CH}(\text{CH}_2 \cdot \text{CO}_2\text{H}) \cdot \text{CH}_2 \\ \text{NH} \text{---} \text{CO} \end{matrix}$ , is obtained, crystallising in silky needles melting at  $183^{\circ}$ ; its *methyl* ester melts at  $111^{\circ}$ ; the *copper* salt is a pale green precipitate; the *silver* salt is soluble in hot water.

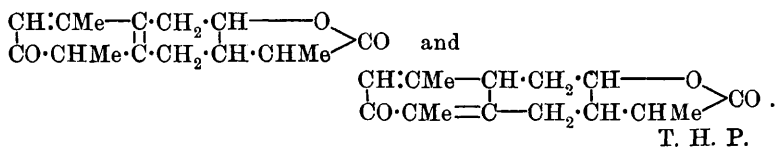
When 2:4-dinitrophenylglutaric acid is reduced with ammonium sulphide,  $\beta$ -4-amino-2-nitrophenylglutaric acid is formed, crystallising in reddish-yellow leaflets which melt and decompose at  $206.5^{\circ}$ .

7-Nitrohydrocarbostyryl-4-acetic acid is obtained if alcoholic stannous chloride is used as the reducing agent; it forms yellow crystals melting at  $185.5^{\circ}$ ; its *methyl* ester crystallises in golden-yellow needles melting at  $125^{\circ}$ , is soluble in alkalis, and forms a reddish-yellow *silver* salt. If the dinitro-acid is reduced with excess of stannous chloride,  $\beta$ -2:4-di-aminophenylglutaric acid is formed; its *copper* salt crystallises with  $1H_2O$ .

K. J. P. O.

**Yellow Santonin (Chromosantonin).** By CLEMENTE MONTE-MARTINI (*Gazzetta*, 1902, 32, i, 325—366).—The author has made an extended study of the properties of the yellow compound formed by the action of sunlight on santonin and of its derivatives. The transformation is unaccompanied by change in weight, and the yellow compound has the same percentage composition and the same molecular weight as unaltered santonin; the change is a complete one and not merely superficial. Chromosantonin yields derivatives distinguishable from those of santonin by their different rotatory powers and by their yellowish tint. Chromosantonin and some of its coloured derivatives are transformed into the corresponding colourless forms by repeated crystallisation. Those derivatives of chromosantonin which contain the same number of carbon atoms, and during the formation of which a change takes place in the molecular nucleus, as, for example, santonous and santoninic acids, are identical with those prepared from santonin. Chromosantonin retains the ketonic and lactonic functions of santonin, but in presence of reducing agents, such as stannous chloride, it reacts much more readily than santonin but gives the same products as the latter. Chromosantonin is more easily oxidised than santonin, and the products obtained from the two compounds are quite different.

The author discusses the various structural formulæ possible for the chromosantonin molecule, which he considers to have one of the two following constitutions:

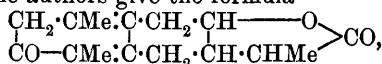


T. H. P.

**Constitution of Photosantonin and isoPhotosantonin Acids.** By LUIGI FRANCESCONI and L. VENDETTI (*Gazzetta*, 1902, 32, i, 281—322).—The authors discuss the work of previous investigators on these two acids and from a consideration of such work and of some new results

obtained by them, they arrive at the following new formulæ for the acids: Photosantonic acid,  $\text{CHMe}_2 \cdot \text{C} : \text{CH} \cdot \text{CH} \cdot \text{OH}$   
 $\text{CO}_2\text{H} \cdot \text{CHMe} \cdot \text{C} : \text{CH} \cdot \text{CH} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$ ;  
 isophotosantonic acid,  $\text{OH} \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{C} : \text{CH} \cdot \text{CH} \cdot \text{OH}$   
 $\text{O} : \text{CH} \cdot \text{CHMe} \cdot \text{C} : \text{CH} \cdot \text{CH} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$

To santonin, the authors give the formula



and they explain the formation of photosantonic and isophotosantonic acids by the action of light as due to the transference of the double linking of the nucleus of the santonin molecule containing the carbonyl group to the other nucleus to which the lateral propionic chain is attached; in the new compound thus formed, the first-named nucleus is then severed and the elements of water taken up, the lactones of photosantonic and isophotosantonic acids being thus obtained. The yellow colour which is temporarily formed during the transformation of santonin into these two lactones, but which disappears when the change is complete, is assumed to be due to the formation of the intermediate compound just referred to.

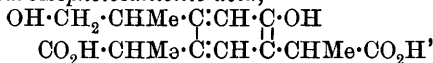
Besides repeating work previously published, the authors have obtained the following new compounds.

*isoPhotosantoniac oxime*,  $\text{C}_{15}\text{H}_{22}\text{O}_4 \cdot \text{NOH}$ , separates in small, rhombohedral crystals which soften at  $130^\circ$ , melt at  $151^\circ$  and are soluble in acetic acid and to a slight extent in alcohol or ether; it has  $[\alpha]_D +170.30^\circ$ . When boiled with acetic anhydride and acetyl chloride, it yields a condensation product,  $\text{C}_{30}\text{H}_{36}\text{O}_5\text{N}_2$ , separating from chloroform in small scales which decompose at  $279^\circ$  and are slightly soluble in ethyl acetate or ethylene bromide.

*isoPhotosantonolactone oxime*,  $\text{C}_{15}\text{H}_{20}\text{O}_3 \cdot \text{NOH}$ , crystallises from ethyl acetate in shining needles melting and decomposing at  $220^\circ$ . Its *acetyl* derivative,  $\text{C}_{17}\text{H}_{23}\text{O}_5\text{N}$ , separates from acetic anhydride solution in square, blunt-angled crystals melting at  $170^\circ$  and is soluble in alcohol, ethyl acetate, or acetic anhydride.

*isoPhotosantonolactone phenylhydrazone*,  $\text{C}_{15}\text{H}_{21}\text{O}_4 \cdot \text{N}_2\text{HPh}$ , separates from ethyl acetate in long, straw-coloured crystals which melt and decompose at  $239^\circ$ .

*Hydroxydehydroisophotosantoniac acid*,

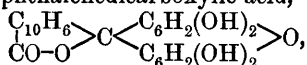


prepared by oxidising isophotosantoniac acid with acid permanganate solution, is deposited from ethyl acetate in shining, prismatic crystals melting at  $283\text{--}284^\circ$  and is slightly soluble in alcohol, benzene, chloroform, or solutions of alkali or alkaline earth hydroxides. Its *acetyl* derivative,  $\text{C}_{17}\text{H}_{22}\text{O}_7$ , separates from ethyl acetate in prismatic crystals which melt at  $251^\circ$  and are soluble in alcohol or chloroform; it has  $[\alpha]_D +58.13^\circ$ . The *barium* salt,  $\text{C}_{15}\text{H}_{28}\text{O}_6\text{Ba}$ , was prepared and analysed.

T. H. P.

**Dihydroxyfluoresceins and Dihydroxyeosins.** By CARL LIEBERMANN and F. WÖBLING (*Ber.*, 1902, 35, 1782—1788).—The *dihydroxy-*

*fluorescein* of 1 : 2-naphthalenedicarboxylic acid,



is prepared by heating together for 2—3 hours at 205—210° the anhydride of naphthalene-1 : 2-dicarboxylic acid and hydroxyquinol, and crystallising the crude product from alcohol ; it separates as a reddish-brown powder readily soluble in glacial acetic acid. The substance dissolves in solutions of the alkali hydroxides and ammonium carbonate, in the latter case, the red solution has a yellowish-green fluorescence ; it is sparingly soluble in boiling water, but dissolves in cold concentrated sulphuric acid to a yellow solution, which, on warming, becomes blue and yields a cerulean blue derivative on dilution with water, this product being also soluble in alkali hydroxides.

The *dibromodihydroxyfluorescein* of 1 : 2-naphthalenedicarboxylic acid,  $\text{C}_{24}\text{H}_{12}\text{O}_7\text{Br}_2$ , produced by the action of bromine on the preceding compound dissolved in glacial acetic acid, crystallises from acetone in white needles melting at 85°. These colourless needles probably consist of an unstable compound with acetone of crystallisation ; on drying at 60° they become golden-yellow and then melt and decompose at 220—230°.

*Dihydroxydimethoxyfluorescein*,  $\text{C}_{22}\text{H}_{16}\text{O}_9$ , prepared from hemipinic anhydride and hydroxyquinol, separates from its alcoholic solution on adding water as a light red powder.

The *dihydroxyfluorescein*,  $\text{C}_{19}\text{H}_{11}\text{O}_7\text{N}$ , of quinolinic acid is obtained by heating quinolinic anhydride and hydroxyquinol at 150° (compare Graebe and Philips, Abstr., 1893, i, 670 ; Philips, Abstr., 1895, i, 572).

The *dihydroxyfluorescein* of diphenyltetrenecarboxylic acid is a brick-red powder prepared by melting together hydroxyquinol and the anhydride of diphenyltetrenecarboxylic acid at 220—230° ; it is soluble in glacial acetic acid, alcohol, or acetone, but insoluble in water, chloroform, or benzene ; the alcoholic solution has a greenish-yellow fluorescence. The compound yields a well-defined, crystalline bromo-derivative.

The preceding substituted fluoresceins and eosins have been examined spectroscopically, and also as dyeing agents for mordanted textile fabrics with the view of ascertaining the effect of substitution on the tinctorial properties of the compounds. The spectroscopic results are tabulated ; the account of the dyeing experiments cannot be suitably abstracted.

G. T. M.

**Action of *p*- and *m*-Nitrobenzaldehyde on Vanillin.** By M. Rogoff (*Ber.*, 1902, 35, 1961—1964).—*p*-Nitrobenzylidenedivanillin,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}[\text{C}_6\text{H}_2(\text{OH})(\text{OMe})\cdot\text{CHO}]_2$ , prepared by heating vanillin and *p*-nitrobenzaldehyde with zinc chloride, is precipitated in flakes on diluting a solution in acetone, is very sparingly soluble in most solvents, but dissolves in alkalis to a yellow solution, melts and decomposes at 276° (corr.), and reduces cold ammoniacal silver and hot Fehling's solution. The *hexa-acetate*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}[\text{C}_6\text{H}_4(\text{OAc})(\text{OMe})\cdot\text{CH}(\text{OAc})_2]_2$ , crystallises from much alcohol in slender, microscopic prisms, is readily soluble in most solvents, and melts at 205·5—207° (corr.).

*m*-Nitrobenzylidenedivanillin crystallises from hot dilute acetic acid in microscopic needles, melts and decomposes at  $266.5^{\circ}$  (corr.), reduces cold ammoniacal silver solutions only slowly, and hot Fehling's solution not at all. The *hexa-acetate* crystallises from alcohol in small prisms and melts at  $154$ — $155^{\circ}$  (corr.). The bis-*phenylhydrazone*,  $C_{35}H_{31}O_6N_5$ , crystallises from hot dilute alcohol and melts and decomposes at  $226^{\circ}$  (corr.).  
T. M. L.

**Benzoin.** By EMIL KNOEVENAGEL and J. ARNDTS (*Ber.*, 1902, 35, 1982—1990. Compare Zinin, *J. pr. Chem.*, 1866, 98, 495; Limpricht and Jena, *Annalen*, 1870, 155, 89; Klinger, *Abstr.*, 1886, 888).—Benzoin is not readily acted on by aqueous potassium hydroxide even when warm and as concentrated as 30 per cent., provided air is excluded. More concentrated alkali (60—80 per cent.), even when air is not present, converts the benzoin into benzyl alcohol and benzoic acid. The best yield of benzyl alcohol, namely, 40 per cent. of the benzoin, is obtained when the alcohol is removed as quickly as formed by the aid of steam at  $180$ — $200^{\circ}$ , or when the temperature is only raised to  $120$ — $130^{\circ}$  and the reaction not allowed to proceed for too long a time. Prolonged action of the alkali at both high and low temperatures lessens the yield of alcohol, and secondary products, namely, stilbene hydrate and hydrobenzoin, are produced together with a substance,  $C_{18}H_{15}O_2$ , probably diethylcarbobenzoic acid (Limpricht and Schwanert, *Annalen*, 1870, 155, 66). It would appear that these secondary products are due to the reducing action of the alcohol on the benzoin, the alcohol itself being oxidised to benzaldehyde, which is then converted by the alkali into benzyl alcohol and benzoic acid.

The chief products formed when benzoin is heated with solid potassium hydroxide are benzyl alcohol, deoxybenzoin, benzhydrol, benzyldeoxybenzoin, and benzoic and benzoic acids. The action of alkali on other ketones is being investigated.  
J. J. S.

**Action of Nitric Acid on Quinone.** By FAUSTO SESTINI (*Gazzetta*, 1902, 32, i, 322—324).—It was stated by Schoonbroodt in 1861 that the action of nitric acid on quinone yields oxalic and picric acids. The author, however, has not been able to find any trace of picric acid in the products of this reaction. When concentrated nitric acid is employed, small quantities of aromatic nitro-compounds are obtained, whilst with dilute acid the quinone is not completely oxidised.

T. H. P.

**Hystazarin.** By CARL LIEBERMANN and W. HOHENEMSER (*Ber.*, 1902, 35, 1778—1781. Compare this vol., i, 475).—The properties ascribed to hystazarin by Lagodzinski and Lorétan (*Abstr.*, 1895, i, 232) do not correspond with those indicated by Liebermann and Schöller (*Abstr.*, 1888, 1203). The dimethyl ether of hystazarin, produced from dimethoxybenzoylbenzoic acid, is not readily hydrolysed with concentrated hydrochloric acid at  $110^{\circ}$  for 5—6 hours; the reaction is, however, rendered complete by treatment with 40 parts of the acid at  $200$ — $205^{\circ}$  for 10—20 minutes. The purification of hystazarin by repeated extraction with hot toluene is absolutely essential, for, during hydrolysis at the higher temperature, this sub-

stance becomes more or less transformed into alizarin, and after  $2\frac{1}{2}$  hours the yield of the latter compound is about 50 per cent.

The alternative method of synthesising hystazarin from catechol and phthalic anhydride leads to the production of six parts of this compound mixed with one part of alizarin.

Alizarin, although scarcely acted on by concentrated sulphuric acid at  $200^\circ$ , is slowly oxidised to purpurin when the temperature is raised to  $225^\circ$ .

G. T. M.

**Derivatives of Anthraquinone obtained in the Action of Sodium Peroxide on Aloins and their Haloid Derivatives.** By EUGÈNE LÉGER (*Compt. rend.*, 1902, 134, 1111—1113).—When a hot solution of barbaloin or isobarbaloin is treated with sodium peroxide, the liquid becomes deep red, and, on acidification, aloë-emodin (m. p.  $224.5$ — $225.5^\circ$ , corr.) is precipitated in both cases; this substance has the composition of a trihydroxymethylanthraquinone, and is identical with the substance obtained by Oesterle (*Abstr.*, 1899, i, 538). The author names this substance isohydroxymethylchrysin. When heated with zinc dust, it yields a hydrocarbon melting at  $208.7^\circ$  (corr.), which, on oxidation, gives an anthraquinonecarboxylic acid; the latter can be converted into anthraquinone.

Chlorobarbaloin and chloroisobarbaloin are converted by sodium peroxide into tetrachloroisohydroxymethylchrysin,  $C_{15}H_6O_5Cl_4$ , crystallising in reddish-orange needles and melting at  $229$ — $231^\circ$  (corr.); on heating with acetic anhydride and acetyl chloride, a triacetyl derivative is obtained which crystallises in pale yellow needles melting at  $270$ — $271^\circ$  (corr.). The corresponding tetrabromo-compound is obtained from bromobarbaloin and crystallises in cinnabar-red needles melting at  $264$ — $266^\circ$  (corr.).

By the action of sodium peroxide on nataloin or homonataloin, methylnataloe-emodin (dihydroxymethoxymethylanthraquinone),  $C_{16}H_{12}O_5$ , is obtained, which crystallises in yellowish-orange needles melting at  $238^\circ$  (corr.); it dissolves in alkalis with a yellowish-orange and in sulphuric acid with a violet coloration; an anthraquinonecarboxylic acid can be obtained from it. When heated with hydrochloric acid at  $170^\circ$ , it is converted into a compound,  $C_{15}H_{10}O_5$  (?), which crystallises, with  $1H_2O$ , in dark reddish-orange needles melting at  $220.5^\circ$  (corr.), and gives with sodium hydroxide a violet, and with sulphuric acid a gooseberry-red, coloration. This compound is named nataloe-emodin.

Optically active substances having the properties of pentoses are formed, together with the compounds just described, by the action of sodium peroxide on the aloins.

K. J. P. O.

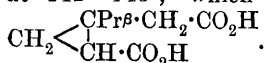
**Decomposition of Cevadine [Veratrine] in Alcoholic Solution by Hydrogen Chloride.** By PAUL HORST (*Chem. Zeit.*, 1902, 26, 334).—When hydrogen chloride is passed into an alcoholic solution of veratrine, ethyl tiglate (b. p.  $151$ — $152^\circ$ ) is obtained, which on hydrolysis yields tiglic acid (m. p.  $62$ — $63^\circ$ ). The tiglic acid is not produced from the angelic acid first formed, as the latter, under the same conditions, is not converted into tiglic acid (compare Wright and Luff, *Trans.*, 1878, 33, 338; Ahrens, *Abstr.*, 1890, 1448; Freund and Schwarz

Abstr., 1899, i, 464). Some of these authors have suggested that angelic acid is the first product of the hydrolysis of veratrine, and is subsequently converted into tiglic acid.

K. J. P. O.

**Sabinenes.** By FRIEDRICH W. SEMMLER (*Ber.*, 1902, 35, 2045—2049. Compare Abstr., 1900, i, 452).—When sabinene ketone,

$\text{CH}_2 \begin{array}{c} \text{CPr}^\beta \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH} - \text{CO} \end{array} \text{CH}_2$ , is oxidised with an alkaline solution of bromine, there is obtained, together with bromoform, an acid melting at 142—143°, which proved to be tanacetonedicarboxylic acid,



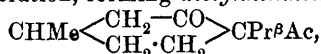
The semicarbazone of sabinene ketone does not regenerate the ketone when warmed with 25 per cent. sulphuric acid, but a liquid hydrocarbon,  $\text{C}_9\text{H}_{14}$ , is formed, which boils at 165—166°, and has a sp. gr. 0.839 at 20°, and  $n_D$  1.4732. This substance is regarded as having

the constitution  $\text{CH}_2 \cdot \text{CMe} \cdot \text{CH} \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CMe} : \text{CH} \end{array}$ .

On reducing sabinene ketone with sodium and alcohol, *sabinene alcohol*,  $\text{C}_9\text{H}_{16}\text{O}$ , is obtained; in attempting to oxidise the alcohol again to the ketone, the hydrocarbon just described was mainly obtained.

K. J. P. O.

**Synthesis of Menthone.** By GEORGES LESER (*Compt. rend.*, 1902, 134, 1115—1116).—The potassium derivative of 4-acetyl-1-methyl-3-cyclohexanone,  $\text{CHMe} \begin{array}{c} \text{CH}_2 - \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{CHAc}$ , condenses with isopropyl iodide in alcoholic solution, forming *acetylmenthone*,



which is a liquid with a faint odour, boiling at 133—135° under 13 mm. pressure, and has a sp. gr. 0.967 at 15° and  $n_D$  1.45737. When boiled with methyl alcoholic potassium hydroxide, menthone is obtained boiling at 207—208°; the *semicarbazone*,  $\text{C}_{11}\text{H}_{21}\text{ON}_3$ , melts at 179—180°, and the oxime at 98—99°.

K. J. P. O.

**Ethereal Oils.** By SCHIMMEL & Co. (*Chem. Centr.*, 1902, i, 1058—1060; from *Geschäftsber.*, April, 1902. Compare Abstr., 1901, i, 394).—Oil of citronella from Ceylon does not contain citronellol but *d*-citronellol has been isolated from the Java oil by treatment with phthalic anhydride. The citronellol obtained from the phthalate boils at 103° under 5 mm. pressure, and has the sp. gr. 0.8618 at 15°,  $[\alpha]_D + 2^\circ 17'$ , and  $n_D$  1.45704 at 22°.

The presence of pinene has not yet been detected in lemon oil (compare Burgess and Child, this vol., ii, 232).

The oil prepared from *Eucalyptus pulverulenta* has a sp. gr. 0.9217 at 15°,  $[\alpha]_D + 1^\circ 4'$ , and is soluble in 2 volumes of 70 per cent. alcohol.

In one sample of oil of lavender, adulteration with benzoic acid was detected.

Oil of cloves contains methyl *n*-amyl ketone and methyl benzoate,



the former boils at 151—153° and has a sp. gr. 0.8223 at 15°. The sp. gr. of eugenol containing water was found to be 1.0725, that of the anhydrous compound being 1.0716 at 15°.

Cinnamon oil from Ceylon contains methyl *n*-amyl ketone, furfuraldehyde, pinene, cymene, benzaldehyde, nonaldehyde, cuminaldehyde, linalool, and caryophyllene,—hydrocinnamaldehyde and linaloyl *iso*-butyrate are also probably present in the oil.

Oil from *Artemisia variabilis* from Reggio has the odour of petit-grain oil, a sp. gr. 0.9115 at 15°,  $[\alpha]_D - 9^\circ 20'$ , and is partially soluble in alcohol; its saponification number is 15.5, whilst that of the acetyl derivative is 49.1.

Oil from the leaves, branches, and fruit of the mandarin tree or "petitgrain mandarinier" of the South of France has an odour like that of neroli and an intense blue fluorescence; it has a sp. gr. 1.005 at 15°, rotatory power  $+7^\circ 19'$ , saponification number 159.1, and is soluble in 9 volumes of 80 per cent. alcohol.

Oil of toona-wood from Nicaragua has a sp. gr. 0.9212 at 15°,  $[\alpha]_D - 46^\circ 50'$ , and consists mainly of cadinene. Cadinene hydrochloride melts at 116.5—117° and has  $[\alpha]_D - 1^\circ 36'$  in 5 per cent. ethereal solution. Cadinene, prepared from the hydrochloride, boils at 128—130° under 4 mm. pressure and has a sp. gr. 0.9244 at 15° and  $[\alpha]_D - 99^\circ 6'$ . Pure safrole solidifies at 11.2° and has a sp. gr. 1.1058—1.1060 at 15° and  $n_D 1.53917$ .  
E. W. W.

**Oil of Coffee.** By ERNST ERDMANN (*Ber.*, 1901, 35, 1846—1854).—The oil is best obtained by distilling roasted coffee with slightly superheated steam, and may readily be separated into an indifferent portion, amounting to about 58 per cent. of the whole, and an acid portion which amounts to 42 per cent. of the whole and consists of a valeric acid, probably  $\alpha$ -methylbutyric acid. The indifferent portion contains about 50 per cent. of furfuryl alcohol, together with a number of phenols. The fraction which contains the characteristic odorous constituent of the oil boils at 93° under 13 mm. pressure and contains 9.71 per cent. of nitrogen. It is only obtained in extremely small quantity, the yield being about 0.89 gram from 65 kilos. of coffee, and possesses in a marked degree the delicate aroma of the coffee. The aroma of coffee is produced when caffetannic acid, caffeine, and cane sugar are gently heated together, but not when any one of these constituents is omitted.  
A. H.

**Constituents of Galanga Oil.** By J. SCHINDELMEISER (*Chem. Zeit.*, 1902, 26, 308).—The oil boiled at 170—275°, had a sp. gr. 0.91 at 20°, a rotatory power  $-2^\circ 27'$  in a 100 mm. tube, and  $n_D 1.4663$  at 20°. Pinene, cineol, and possibly cadinene are present in the oil; in the fraction 230—240°, a new hydrocarbon is found, the *hydrochloride* of which,  $C_{15}H_{24} \cdot 2HCl$ , crystallises in leaflets, is optically inactive, and melts at 51°.  
K. J. P. O.

**Resina Pini from Siebenbürgen (from Picea Vulgaris).** By ALEXANDER TSCHIRCH and M. KOCH (*Arch. Pharm.*, 1902, 240, 272—287, Compare Abstr., 1901, i, 91).—The resin contained 20 per

cent. of woody and other impurities; purified from these, it had acid and saponification number 126 and iodine number 54·4. By distilling the resin, formic, acetic, and succinic acids were obtained. A small quantity of a *bitter-substance* is present in the resin.

From an ethereal solution of the resin 1 per cent. aqueous ammonium carbonate extracted *picipimarinic acid*,  $C_{12}H_{20}O_2$ , which is amorphous, melts at 132—135°, and has acid and saponification number 288, corresponding with monobasicity, and iodine number 64·4, corresponding with the formation of a moniodo-derivative.

One per cent. aqueous sodium carbonate solution then extracted a mixture of acids. From a solution of these in a mixture of methyl and ethyl alcohols, piceapimaric acid crystallises identical with that obtained from Jura turpentine; it is optically inactive and has acid and saponification number 187·5, corresponding with monobasicity, and iodine number 35·4, corresponding with the formation of a moniodo-derivative. From the mother liquor,  $\alpha$ - and  $\beta$ -*picipimarolic acids*,  $C_{18}H_{28}O_2$ , were isolated; these are amorphous and melt at 90—96° and 88—94° respectively; they have acid and saponification number 204, corresponding with monobasicity, and iodine number 46·35, corresponding with the formation of a moniodo-derivative; their lead salts are respectively insoluble and soluble in alcohol.

Aqueous potassium hydroxide extracted nothing from the remaining ethereal solution, but a reddish *colouring-matter* separated at the junction of the two liquids.

When the ether was distilled off and the residue distilled with steam, an *essential oil* came over which boiled at 175—180° and had the sp. gr. 0·870, whilst an amorphous substance of an indifferent character, *picoresen*,  $C_{19}H_{30}O$ , remained behind. A little of this resin separated when the ethereal solution of the resin was extracted with ammonium carbonate.

In 100 parts of the (purified) drug there were contained: picipimarinic acid, 3; piceapimaric acid, 2;  $\alpha$ - and  $\beta$ -picipimarolic acids, 47; essential oil, 30; picoresen, 15; bitter-substance (succinic acid), colouring matter, water and impurities, 3. C. F. B.

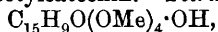
**West Indian Sandalwood Oil.** By ERNST DEUSSEN (*Arch. Pharm.*, 1902, 240, 288—293. Compare Abstr., 1900, ii, 579).—By suitable treatment of the oil, chiefly fractionation, oils were obtained which had respectively: boiling point under 26 mm. pressure, 153—154°, 155—156° (260—261° and 257—259° under atmospheric pressure), 150—143°, 139—141°; sp. gr. 0·925, 0·914, 0·903, 0·902 at 15°, and specific rotation,  $[\alpha]_D +54^\circ$ ,  $+(11-16^\circ)$ ,  $-2\frac{1}{2}^\circ$ ,  $-5\frac{1}{4}^\circ$ . The first forms with hydrogen chloride a crystalline hydrochloride melting at 117—118°, and is probably *r*-cadinene; the second may be galipene; the last two are possibly identical, and may be caryophyllene or guajene.

C. F. B.

**Caoutchouc.** II. By CARL O. WEBER (*Ber.*, 1902, 35, 1947—1951).—Purified Para rubber dissolved in benzene is converted by nitrosyl chloride, produced by the interaction of amyl nitrite and acetyl chloride, into a stiff jelly which soon decomposes, evolving gas

and giving a solution of apparently unchanged rubber. Nitrogen peroxide, evolved from lead nitrate, precipitates from a solution of caoutchouc in benzene, a brownish-yellow, amorphous powder, which is very soluble in acetone, and is precipitated from it by water in the form of a bright yellow mass having the composition  $C_{10}H_{16}O_4N_2$ . Balata and guttapercha give compounds of the same composition, but that obtained from the former is only sparingly soluble in acetone. These substances easily dissolve in alkalis; the *sodium* derivative,  $C_{10}H_{15}O_4N_2Na$ , was obtained as a brown, flocculent mass by dissolving the substance in concentrated methyl alcoholic sodium methoxide and diluting with absolute alcohol; the corresponding *silver* derivative,  $C_{10}H_{15}O_4N_2Ag$ , is precipitated by silver nitrate from an aqueous solution of the sodium compound as a brownish jelly. W. A. D.

**Catechin.** By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1901, 35, 1867—1869).—Catechin appears to have the formula  $C_{15}H_{14}O_6 \cdot 4H_2O$ . The penta-acetyl compound,  $C_{15}H_9O(OAc)_5$ , can be readily prepared by the direct action of acetic anhydride and sodium acetate, and was previously described by Liebermann and Tauchert (*Abstr.*, 1881, 52) as diacetylcatechin. *Tetramethylcatechin*,



prepared by the action of methyl sulphate on catechin, crystallises in needles melting at 142—143°. Pure sulphuric acid yields a yellow solution with a green fluorescence, but if nitrous acid be present a deep reddish-violet coloration is produced. *Acetyltetramethylcatechin* crystallises in colourless needles melting at 92—93°. The tetramethyl compound is converted by oxidation with cold chromic acid solution into *trimethylcatechone*,  $C_{18}H_{18}O_7$ , which crystallises in orange-coloured needles and melts and decomposes at 210°. A. H.

**Furfuryl Alcohol.** By ERNST ERDMANN (*Ber.*, 1901, 35, 1855—1862).—Furfuryl alcohol is best prepared by a modification of Schiff's method (*Ber.*, 1886, 19, 2154), furfuraldehyde being gradually added to aqueous sodium hydroxide and the product distilled with steam. It forms a colourless liquid of characteristic odour and bitter taste, boils at 68—69° under 10 mm. and 170—171° under 758 mm. pressure, and has a sp. gr. 1.1351 at 20°/20°. The pure substance mixes with water in all proportions, but the solution gradually separates into two layers; the nature of this decomposition has not yet been ascertained. The pure compound, moreover, does not form the compound with aniline which was obtained by Schiff. When brought into contact with aldehydes and hydrochloric acid, a bluish-green coloration is produced, and this reaction is also given with a pine wood splinter moistened with hydrochloric acid. Furfuraldehyde, however, produces with it a bluish-violet coloration.

*Furfuryl diphenylcarbamate*,  $NPh_2 \cdot CO \cdot O \cdot CH_2 \cdot C_4H_9O$ , obtained by heating the alcohol with diphenylcarbamide chloride and pyridine, forms lustrous, faintly yellow needles melting at 97.5—98°. The corresponding *furfuryl carbamate*,  $NH_2 \cdot CO \cdot O \cdot CH_2 \cdot C_4H_9O$ , crystallises in slender needles melting at 50°. It is accompanied by another compound which melts and decomposes at 170°.

The physiological effect of the alcohol on rabbits, investigated by E. Harnack, is that respiration is paralysed, the lethal dose being 0.5—0.6 gram per kilo. A. H.

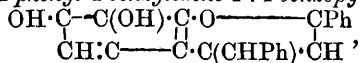
**Naphthafurfuran from Coal Tar.** By JOHANNES BOES (*Zeit. öffentl. Chem.*, 1902, 8, 151—152. Compare Abstr., 1897, i, 526; 1900, i, 650).—After being freed from phenols and bases, the fraction of coal tar boiling at 282—292° is alternately redistilled, treated with picric acid, and the picrate decomposed by steam. On cooling, the purified fraction, boiling at 282—286°, deposits  $\beta$ -naphthafurfuran (m. p. 60—61°, b. p. 284—286°). The liquid part of the fraction is  $\alpha$ -naphthafurfuran, which has a sp. gr. 1.1502 at 15°, and boils at 282—284°.

The yields are 2 grams of  $\beta$ - and 0.5 gram of  $\alpha$ -naphthafurfuran from 2 kilos. of the original fraction boiling at 282—292°. G. Y.

**Polyvalent Oxygen.** By PAUL WALDEN (*Ber.*, 1902, 35, 1764—1772. Compare this vol., i, 169).—This communication contains a short summary of the bibliography of quadrivalent oxygen, a discussion of the univalent and sexavalent character of this element, and an account of electrical experiments indicating that dimethylpyrone is not only a basic, but also an acidic, substance.

The electrical conductivity of dimethylpyrone in hydrazine hydrate solution at 0° varies from 15.2 to 23.9 units according as the concentration diminishes from 1 gram-mol. in 100 litres to the same amount in 420 litres. A solution of a true binary salt, namely, tetraethylammonium iodide, having a similar concentration has only double the conductivity, and this result serves to show that a salt has been produced between the hydrazine and the dimethylpyrone. G. T. M.

**1:4-Benzopyranol Derivatives from Phenylacetylacetophenone and Trihydric Phenols and Orcinol.** By CARL BÜLOW and HANS GROTHOWSKY (*Ber.*, 1902, 35, 1799—1810. Compare Abstr., 1901, i, 400, 559, 603; this vol., i, 112—113).—The *hydrochloride* of 7:8-dihydroxy-2-phenyl-4-benzylidene-1:4-benzopyranol,



is prepared by passing hydrogen chloride into a mixture of phenylacetylacetophenone and pyrogallol dissolved in acetic acid; it crystallises with 1H<sub>2</sub>O in reddish-brown, lustrous needles decomposing at 245°, and dissolves in concentrated sulphuric acid with a yellow coloration; this solution does not fluoresce. The *picrate* crystallises in reddish-brown, lustrous leaflets which sinter on heating and melt at 193°. On heating the hydrochloride with sodium acetate in acetic acid solution, the *diacetyl* derivative of the benzopyranol is obtained; it crystallises in pale yellow needles, which soften at 156° and melt and decompose at 160°. The *dibenzoyl* derivative, prepared from the hydrochloride, crystallises in yellow needles melting and decomposing at 178°. The *dimethoxy*-derivative, prepared by heating the hydrochloride with sodium and methyl iodide in methyl alcoholic solution,

crystallises in long, yellow needles melting and decomposing at 141—143°.

The *hydrochloride* of 5:7-dihydroxy-2-phenyl-4-benzylidene-1:4-benzopyranol,  $\text{HO}\cdot\text{C}\cdot\text{CH}\text{---}\text{C}\cdot\text{O}\text{---}\text{CPh}$   
 $\text{CH}\cdot\text{C}(\text{OH})\cdot\text{C}\cdot\text{C}(\text{CHPh})\cdot\text{CH}$ , is obtained from phenyl-acetylacetophenone and phloroglucinol; it forms orange-red crystals which sinter at 175°, melt and decompose at 241° and contain 1H<sub>2</sub>O; when boiled with concentrated aqueous potassium hydroxide, it is decomposed into acetophenone, dihydroxyphenyl benzyl ketone (?), and benzoic and phenylacetic acids.

The *picrate* crystallises in orange-red needles decomposing at 205°; the *diacetyl* derivative crystallises in yellowish-white needles which decompose at 148—149.5°; the *dimethoxy*-derivative is prepared by addition of methyl sulphate to an alkaline solution of the benzopyranol; it crystallises in yellow needles melting and decomposing at 140—142°.

The *hydrochloride* of 6:7-dihydroxy-2-phenyl-4-benzylidene-1:4-benzopyranol,  $\text{OH}\cdot\text{C}\cdot\text{CH}\cdot\text{C}\cdot\text{O}\text{---}\text{CPh}$   
 $\text{OH}\cdot\text{C}\cdot\text{CH}\cdot\text{C}\cdot\text{C}(\text{CHPh})\cdot\text{CH}$ , is prepared from hydroxy-quinol and phenylacetylacetophenone, and crystallises in small, brown leaflets, with 1½H<sub>2</sub>O, melting and decomposing at 169°. The benzopyranol is obtained from the hydrochloride by the addition of aqueous sodium acetate to its alcoholic solution; it forms ruby-red crystals decomposing at about 170° and shows a faint green fluorescence when dissolved in sulphuric acid. The *sulphate* crystallises in reddish-brown needles with 3H<sub>2</sub>O, begins to melt at 150°, and is completely liquefied at 183°; the *platinichloride* is a yellowish-brown, crystalline precipitate; the *picrate* forms brownish-red crystals melting and decomposing at 198°; the *diacetyl* derivative crystallises in lemon-yellow leaflets or needles and dissolves in sulphuric acid with a green fluorescence.

The *hydrochloride* of 7- (or 5-)hydroxy-2-phenyl-4-benzylidene-5- (or 7-)methyl-1:4-benzopyranol is prepared from phenylacetylacetophenone and orcinol, and crystallises with 4H<sub>2</sub>O in orange-red needles; the *base* was only obtained as a brown precipitate which gave a yellow, fluorescent solution in sulphuric acid; the *picrate* forms crystals decomposing at 181°; the *cobalticyanide* crystallises in lustrous, red leaflets, which lose their colour at 190° and decompose at 200°. The *acetyl* derivative, prepared by treating the hydrochloride with acetic anhydride and pyridine, crystallises in yellow needles melting at 134°; the *benzoyl* derivative forms yellow needles decomposing at 134—136°; the *methoxy*-derivative, yellow leaflets melting at 141—145°.

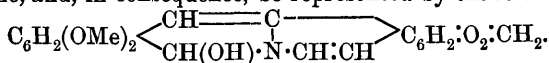
K. J. P. O.

**Constitution of Berberine.** By JOHANNES GADAMER (*Chem. Zeit.*, 1902, 26, 291—292; 385. Compare this vol., i, 273).—The formula for berberine (*loc. cit.*), which represents the alkaloid as a quaternary base, is confirmed by later observations. On treating a solution of acid berberine sulphate with barium hydroxide, a brownish-red, strongly alkaline solution of the free base, *berberinium hydroxide*, C<sub>20</sub>H<sub>19</sub>O<sub>6</sub>N, is obtained; with excess of sodium hydroxide, this solution yields

*berberinaldehyde*,  $\text{CHO} \cdot \text{C}_8\text{H}_8\text{O}_2 \cdot \text{CH} : \text{C} \begin{array}{c} \text{—————} \\ | \\ \text{NH} \cdot \text{CH} : \text{CH} \end{array} > \text{C}_6\text{H}_2 \cdot \text{O}_2 \cdot \text{CH}_2$ , which

melts at  $144^\circ$ , and on warming with water is reconverted into berberinium hydroxide. By the action of concentrated sodium hydroxide, berberinaldehyde (2 mols.) yields *dihydroberberine*,  $\text{C}_{20}\text{H}_{21}\text{O}_5\text{N}$  (1 mol.), and oxyberberine,  $\text{C}_{20}\text{H}_{19}\text{O}_6\text{N}$  (1 mol.). Dihydroberberine is a yellow, crystalline base melting at  $163\text{--}164^\circ$ , and is the primary alcohol corresponding with the aldehyde berberinal, whilst oxyberberine (m. p.  $198\text{--}199^\circ$ ) is the corresponding carboxylic acid. Dihydroberberine is converted into berberine when exposed to the air.

The second paper states that Roser has suggested that berberinal (*loc. cit.*) may not be an aldehyde, but the pseudoammonium hydroxide of berberine, and, in consequence, be represented by the formula



K. J. P. O.

**Cotarnine.** By MARTIN FREUND and GEORG WULFF (*Ber.*, 1902, **35**, 1737—1739).—*Oxycotarnine*,  $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}(\text{OMe}) \begin{array}{c} \text{CO} - \text{NMe} \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$ , the principal product of the oxidation of cotarnine with aqueous potassium permanganate, crystallises from dilute alcohol in colourless prisms, with  $1\text{H}_2\text{O}$ , melting at  $69\text{--}70^\circ$ ; when dry, it melts at  $108^\circ$ . The *platinichloride* melts and decomposes at  $179\text{--}180^\circ$ , and the *aurichloride* melts at  $160^\circ$ . *Bromo-oxycotarnine*,  $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{Br}(\text{OMe}) \begin{array}{c} \text{CO} - \text{NMe} \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$ , obtained by brominating the oxidation product, melts at  $125\text{--}126^\circ$ .

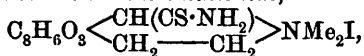
*Cotarnic acid methylimide*,  $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}(\text{OMe}) \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{NMe}$ , is also formed in small quantity along with cotarnic acid in the foregoing oxidation; it melts at  $205\text{--}206^\circ$ . W. A. D.

**Cotarnine.** By MARTIN FREUND and PAUL BAMBERG (*Ber.*, 1902, **35**, 1739—1754).—Cyanohydrocotarnine methiodide (Freund, 1900, i, 248) is converted by warming with very dilute alkali into *hydrocotarnine carboxylamide methiodide*,  $\text{C}_8\text{H}_6\text{O}_3 \begin{array}{c} \text{CH}(\text{CO} \cdot \text{NH}_2) \\ | \\ \text{CH}_2 - \text{CH}_2 \end{array} > \text{NMe}_2\text{I}$ , which crystallises from dilute alcohol in lustrous leaflets, melts at  $235^\circ$ , and on boiling with concentrated potassium hydroxide, gives, by loss of hydrogen iodide, the base  $\text{CH}_2 \cdot \text{CH} \cdot \text{C}_8\text{H}_6\text{O}_3 \cdot \text{CH}(\text{CO} \cdot \text{NH}_2) \cdot \text{NMe}_2$ ; this crystallises from dilute alcohol in aggregates of needles, melts at  $182^\circ$ , and forms a crystalline *hydrochloride*, melting, when dry, at  $207\text{--}208^\circ$ , a *hydriodide* melting at  $184^\circ$ , and a *methiodide* melting at  $195^\circ$ . The *lactone*,  $\text{C}_8\text{H}_6\text{O}_3 \begin{array}{c} \text{CH}(\text{NMe}_2) \\ | \\ \text{CHMe} - \text{O} \end{array} > \text{CO}$ , is obtained by heating the base for 5—10 minutes with aqueous alcoholic hydrogen chloride, and separates from water in white crystals melting at  $168^\circ$ ; it is converted by warm aqueous alkali into the *hydroxy-acid*,

$\text{OH} \cdot \text{CHMe} \cdot \text{C}_8\text{H}_6\text{O}_3 \cdot \text{CH}(\text{NMe}_2) \cdot \text{CO}_2\text{H}$ , which melts at  $207^\circ$  and has both acid and basic properties.

If, in hydrolysing the base, absolute alcoholic hydrogen chloride is employed under pressure at 100°, carbon dioxide is split off and the compound,  $\text{CH}_2:\text{CH}\cdot\text{C}_8\text{H}_6\text{O}_3\cdot\text{CH}_2\cdot\text{NMe}_2$ , formed; it crystallises from water and melts at 229—230°.

*Hydrocotarninethiocarbonamide methiodide,*



obtained by heating cyanocotarnine methiodide for a few minutes with ammonium sulphide, crystallises from water in short, thick, lemon-yellow prisms or long, lustrous needles, melts at 203°, and when boiled with potassium hydroxide solution is converted by loss of hydrogen iodide and hydrogen sulphide into the foregoing base melting at 182°. With dilute aqueous sodium hydrosulphide, on the other hand, cyanocotarnine methiodide gives the same compound, melting at 235°, as was obtained by using sodium hydroxide. The *ammonium base*,  $\text{C}_8\text{H}_6\text{O}_3 \left\langle \begin{array}{c} \text{CH}(\text{OS}\cdot\text{NH}_2) \\ \text{CH}_2\text{---CH}_2 \end{array} \right\rangle \text{NMe}_2\cdot\text{OH}\cdot 2\text{H}_2\text{O}$ , obtained by suspending the thio-compound, melting at 203°, in cold dilute sodium hydroxide, crystallises in nacreous leaflets and melts at 135° when hydrated, at 141—142° when anhydrous.

*Ethylmercaptohydrocotarnine*,  $\text{C}_8\text{H}_6\text{O}_3 \left\langle \begin{array}{c} \text{CH}(\text{SEt})\cdot\text{NMe} \\ \text{CH}_2\text{---CH}_2 \end{array} \right\rangle$ , obtained by adding ethyl mercaptan to cotarnine suspended in ether, separates from the latter in well-formed crystals and melts at 55°; the *methiodide*,  $\text{C}_8\text{H}_6\text{O}_3 \left\langle \begin{array}{c} \text{CH}(\text{SEt})\cdot\text{NMe}_2\text{I} \\ \text{CH}_2\text{---CH}_2 \end{array} \right\rangle$ , with  $1\text{H}_2\text{O}$ , melts at 75—80°, or when dry at 95—100°.

*Ethoxyhydrocotarnine*,  $\text{C}_8\text{H}_6\text{O}_3 \left\langle \begin{array}{c} \text{CH}(\text{OEt})\cdot\text{NMe} \\ \text{CH}_2\text{---CH}_2 \end{array} \right\rangle$ , is obtained by evaporating an absolute alcoholic solution of cotarnine in a vacuum.

For a justification of the preceding formulæ, the original should be consulted.

W. A. D.

**The Existence of Lysatinine.** By MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1902, 35, 192—195. Compare Hedin, *ibid.*, 1895, 21, 297).—Experiments are described which tend to show that the silver derivative of lysatinine is not a mixture of the silver derivatives of lysine and arginine in molecular proportions as suggested by Hedin.

J. J. S.

**Lupinine.** By RICHARD WILLSTÄTTER and ERNEST FOURNEAU (*Ber.*, 1902, 35, 1910—1926).—The low boiling point of lupinine and its derivatives points to a simpler formula than  $\text{C}_{21}\text{H}_{40}\text{O}_2\text{N}_2$  (Baumert, *Abstr.*, 1881, 831; 1882, 229, 873); the analytical data were found to agree equally well with the formula  $\text{C}_{10}\text{H}_{16}\text{ON}$ , and this was confirmed by cryoscopic measurements of lupinine and benzoyl-lupinine. Lupinine is a tertiary base, contains no methyl groups attached to nitrogen, is saturated, and therefore contains two ring systems, and is not altered by sodium amyloxide in amyl alcohol under conditions which convert tropine into  $\psi$ -tropine. With phenylcarbimide, it forms the *compound*

$(C_{10}H_{18}N)O \cdot CO \cdot NHPh$ , which crystallises from absolute alcohol in glistening prisms and needles, is insoluble in water, and melts at  $94-95^\circ$ ; lupinine therefore contains a hydroxyl group.

*Anhydrolupinine*,  $C_{10}H_{17}N$ , prepared by heating lupinine with acetic and sulphuric acids at  $180^\circ$ , is a colourless oil of unpleasant, narcotic odour, boils at  $216.5-217.5^\circ$  under 726 mm. pressure, is oxidised by potassium permanganate, and apparently by picric acid. The *platinichloride*,  $(C_{10}H_{17}N)_2 \cdot H_2PtCl_6$ , separates from water in reddish-brown crystals, which are stable in air, darkens at  $170^\circ$ , and decomposes at  $216^\circ$ . The *aurichloride*,  $C_{10}H_{17}N \cdot HAuCl_4$ , forms transparent, golden-yellow prisms and, when quickly heated, melts at  $140-141^\circ$ . The *methiodide*,  $C_{10}H_{17}N \cdot MeI$ , forms sharp-edged flakes and decomposes and melts at  $180^\circ$ .

*Lupinic acid*,  $C_9H_{16}N \cdot CO_2H$ , prepared by oxidising lupinine with chromic acid, crystallises from dilute acetone in splendid, long, colourless needles containing  $3H_2O$ . The anhydrous acid, when quickly heated, melts without darkening and without decomposing at  $255^\circ$ , and can be sublimed in a test-tube; it is readily soluble in water or alcohol, but not in dry acetone or ether, does not reduce silver oxide or permanganate, and does not form metallic salts, but gives salts with acids; the *hydrochloride*,  $C_{10}H_{17}O_2N \cdot HCl$ , separates from alcohol in stout, well-developed, prismatic crystals, is very easily soluble in water, and melts and decomposes at  $275^\circ$ ; the *platinichloride*,  $(C_{10}H_{17}O_2N)_2 \cdot H_2PtCl_6 \cdot 3H_2O$ , is readily soluble in water, but crystallises from moist acetone or ether in short, transparent, red prisms, darkens at  $120^\circ$ , and decomposes vigorously at  $235^\circ$ ; the *aurichloride*,  $C_{10}H_{17}O_2N \cdot HAuCl_4$ , is only slightly soluble in cold water, crystallises in long, golden-yellow needles, and melts at  $188^\circ$ . The *methyl ester*,  $C_9H_{16}N \cdot CO_2Me$ , is a colourless, mobile oil, boils at  $131^\circ$  under 15 mm. pressure, has a strong alkaline reaction, is little soluble in cold, and less so in hot, water; the aurichloride was obtained as an oil; the *platinichloride*,  $(C_{11}H_{19}O_2N)_2 \cdot H_2PtCl_6$ , crystallises from hot water in orange-coloured needles, and melts and decomposes at  $210-212^\circ$ ; the *methiodide*,  $C_{11}H_{19}O_2N \cdot MeI$ , forms glistening, white tablets, melts with slight evolution of gas at  $225-226^\circ$ , and is stable towards alkalis, indicating that it is probably derived from a  $\beta$ -amino-acid.

*Methyl-lupuline*,  $C_{10}H_{18}ONMe$ , prepared by distilling lupulinemethyl-ammonium hydroxide under reduced pressure, is a colourless, viscid oil of slight fishy odour, boils at  $145-146^\circ$  under 15 mm. pressure, is soluble in about 50 parts of cold, less so in hot, water, is not very readily volatile with steam, behaves as a tertiary base, reduces potassium permanganate, gives an oily aurichloride and a syrupy platinichloride, and may perhaps contain two isomeric compounds. The *methiodide*,  $[C_{10}H_{18}ONMe_2]I$ , crystallises from alcohol in long, colourless prisms and melts at  $224-225^\circ$ , but the product is not homogeneous, and more than half of it remains as a syrup.

*Dimethyl-lupuline*,  $C_{10}H_{17}ONMe_2$ , boils at  $169-172^\circ$  under 28-29 mm. pressure, and resembles methyl-lupuline. When the ammonium hydroxide of this base is distilled, it loses the whole of the nitrogen as trimethylamine, leaving a compound which behaves as an unsaturated alcohol.

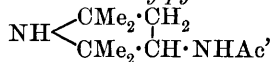


Lupinine probably contains a ring system,  $\text{N} \begin{array}{c} \diagup \text{C}-\text{C} \diagdown \\ \diagdown \text{C} \diagup \\ \diagup \text{C}-\text{C} \diagdown \end{array} \text{C}$ , similar to that which exists in cinchonine. T. M. L.

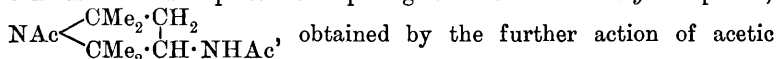
**Conversion of Tropidine into Tropine.** By RICHARD WILLSTÄTTER (*Ber.*, 1901, 35, 1870).—Ladenburg's method for the conversion of tropidine into tropine (this vol., i, 390) depends on the action of dilute acid at 160° on a mixture of  $\alpha$ - and  $\beta$ -bromotropans, and therefore closely resembles that previously employed by the author (*Abstr.*, 1901, i, 744). A. H.

**The Hydropyrrole Series.** By HERMANN PAULY (*Annalen*, 1902, 322, 77—130. Compare *Abstr.*, 1899, i, 773, 872; 1900, i, 357; 1901, i, 607).—3-Amino-2:2:5:5-tetramethylpyrrolidine yields the following derivatives: the *platinichloride*,  $\text{C}_8\text{H}_{18}\text{N}_2 \cdot \text{H}_2\text{PtCl}_6 \cdot 3\text{H}_2\text{O}$ , crystallising in orange-red, twinned prisms, becoming anhydrous at 105°, and decomposing at 215°; the *picrate*,  $\text{C}_8\text{H}_{18}\text{N}_4 \cdot 2\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$ , forming yellow needles melting at 242°, and the *carbamate*,  $\text{C}_9\text{H}_{18}\text{O}_2\text{N}_2$ , separating from ether in white, microscopic needles and sintering and decomposing at 142—145°.

3-Acetyl-amino-2:2:5:5-tetramethylpyrrolidine,



produced on mixing the primary base with cold acetic anhydride, boils at 150—151° under 13—14 mm., and at 155° under 16 mm. pressure; it solidifies in spherical aggregates melting at 70°; its hydrochloride is readily soluble in water and yields a nitrosoamine with nitrous acid; the *aurichloride* dissolves but sparingly in the cold solvent and crystallises in rhombic plates decomposing at 213°. The *diacetyl* compound,



obtained by the further action of acetic anhydride, separates from benzene in small, well-defined crystals and melts at 166—167°. 2:2:5:5-Tetramethyl- $\Delta^3$ -pyrroline forms a soluble hydrochloride and hydriodide; the *picrate* crystallises from alcohol in spherical aggregates of needles melting at 255—256° when rapidly heated and decomposing at 240° when slowly heated. The *aurichloride* separates from aqueous solutions of its generators as an oil solidifying in yellow needles; the *platinichloride*,  $(\text{C}_8\text{H}_{15}\text{N})_2 \cdot \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$ , crystallises from water in oblique, tabular prisms; it becomes anhydrous at 100° and decomposes at 200°. 3-Amino-1:2:2:5:5-pentamethylpyrrolidine furnishes a *picrate*,  $\text{C}_9\text{H}_{20}\text{N}_2 \cdot 2\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$ , crystallising in yellow needles from an alcoholic solution of its generators and melting at 215°; the normal *oxalate*,  $\text{C}_9\text{H}_{20}\text{N}_2 \cdot \text{H}_2\text{C}_2\text{O}_4$ , separates, on adding dry oxalic acid to an ethereal solution of the amine, in small, triangular or hexagonal plates melting at 216°. 3-Acetyl-amino-

1:2:2:5:5-pentamethylpyrrolidine,  $\text{NMe} \begin{array}{c} \diagup \text{CMe}_2 \cdot \text{CH}_2 \\ \diagdown \text{CMe}_2 \cdot \text{CH} \cdot \text{NHAc}' \end{array}$ , boils at 145—146° under 11 mm. pressure and solidifies to a mass of radiating crystals melting at 87°.

The *phenylthiocarbamide*,  $\text{NMe} \begin{array}{l} \diagup \text{CMe}_2 \cdot \text{CH}_2 \\ \diagdown \text{CMe}_2 \cdot \text{CH} \cdot \text{NH} \cdot \text{CS} \cdot \text{NHPh} \end{array}$ , produced by mixing the diamine with phenylthiocarbimide in methyl alcohol, crystallises from this solvent in silky needles and melts at  $146^\circ$ ; its hydrochloride is readily soluble and yields a sparingly soluble aurichloride and platinichloride.

The *a*-thiocarbamate of 3-amino-2:2:5:5-pyrrolidine is readily transformed into its *b*-isomeride on boiling with water for a short time (Abstr., 1901, i, 607). This transformation does not readily occur in the case of the *a*-thiocarbamate of 3-amino-1:2:2:5:5-pentamethylpyrrolidine; this substance, which, when freshly prepared, melts at  $103^\circ$ , becomes altered after two days and then sinters at  $46^\circ$ , effervesces at  $90^\circ$ , and completely decomposes at  $125^\circ$ .

3-Keto-2:2:5:5-tetramethylpyrrolidine (compare Pauly and Boehm, Abstr., 1901, i, 607) forms a soluble *hydrochloride*,  $\text{C}_8\text{H}_{15}\text{ON} \cdot \text{HCl}$ , and *hydriodide* crystallising in needles; the *aurichloride*,  $\text{C}_8\text{H}_{15}\text{ON} \cdot \text{HAuCl}_4$ , separates in light yellow needles and melts at  $178^\circ$ , the *platinichloride* forms orange-coloured, quadratic plates, and the *picrate*,  $\text{C}_8\text{H}_{15}\text{ON} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{OH}$ , crystallises from alcohol in yellow leaflets and melts at  $226^\circ$ .

The *hydrochloride*,  $\text{NH}_2 \begin{array}{l} \diagup \text{CMe}_2 \cdot \text{CH}_2 \\ \diagdown \text{CMe}_2 \cdot \text{CO} \\ \text{O} \end{array} \text{C} \cdot \text{OH} \cdot \text{HCl} \cdot \text{H}_2\text{O}$ , of the amino-acid, obtained by hydrolysing the cyanohydrin of the keto-base with concentrated hydrochloric acid at  $-10^\circ$ , crystallises from water in prisms or hexagonal plates, evolving water at  $120^\circ$  and melting at  $226^\circ$ ; both the hydrochloride and the free acid are readily soluble in water.

3-Hydroxy-2:2:5:5-tetramethylpyrrolidine, obtained by reducing the keto-base with sodium amalgam, yields a *hydrochloride* crystallising in needles readily soluble in water or alcohol, but dissolving very sparingly in boiling acetone. The base,

$\text{C}_8\text{H}_{19}\text{ON} [= \text{NH}_2 \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CHMe}_2 ?]$ , also formed in this reduction and separated from the other product by means of the ready solubility of its hydrochloride in acetone, furnishes a *platinichloride*,  $\text{C}_8\text{H}_{19}\text{ON} \cdot \text{H}_2\text{PtCl}_6$ , crystallising in orange-coloured, rhombic plates containing 1 mol. of alcohol of crystallisation and melting at  $170^\circ$ . This base, when treated with nitrous acid, yields a yellow oil resembling the ethereal nitrites; on oxidation, it gives rise to ammonia and a product boiling at  $150^\circ$  and having an odour resembling that of mesityl oxide.

3-Hydroxy-2:2:5:5-tetramethylpyrrolidine mandelate is a white, resinous product having a powerful mydriatic action.

3-Keto-1:2:2:5:5-pentamethylpyrrolidine,  $\text{NMe} \begin{array}{l} \diagup \text{CMe}_2 \cdot \text{CH}_2 \\ \diagdown \text{CMe}_2 \cdot \text{CO} \end{array}$ , prepared by treating 1:2:2:5:5-pentamethyl- $\Delta^3$ -pyrrolinocarboxylamide with potassium hypobromite, boils at  $187-188^\circ$  under 755 mm. pressure and solidifies to a mass of feathery crystals melting at  $43^\circ$ ; the substance has the odour both of ammonia and camphor, and on exposure to the air assumes a reddish-brown colour. The *hydriodide* crystallises in long needles melting above  $220^\circ$ ; the *platinichloride*

and hydrochloride are both very soluble salts; the *oxime* sublimes in needles soluble in water, alcohol, or ether, and melts at 104°.

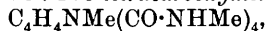
A considerable portion of the experimental part of this communication has already been published; the theoretical part includes a discussion of the genetic relationships of the hydropyrrole derivatives, the connection between the different members of the series being also illustrated by means of a diagram.

G. T. M.

*N*-Methylpyrrolidine- $\alpha_1$ - $\alpha_2$ -dicarboxylic Acid [1-Methylpyrrolidine-2:5-dicarboxylic Acid]. By RICHARD WILLSTÄTTER and RUDOLF LESSING (*Ber.*, 1902, 35, 2065—2073. Compare *Abstr.*, 1899, i, 633; 1900, i, 405; 1901, i, 650; and this vol., i, 266).—*Ethyl  $\alpha\delta$ -dibromoadipate*,  $C_4H_6Br_2(CO_2Et)_2$ , prepared from the corresponding acid, crystallises in colourless prisms or needles melting at 65·5—66·5°, and is converted into 1-methylpyrrolidine-2:5-dicarboxylic acid,

$NMe \begin{array}{c} \text{CH}(CO_2H) \cdot CH_2 \\ | \\ \text{CH}(CO_2H) \cdot CH_2 \end{array}$ , by heating with a dry solution of methylamine in benzene and hydrolysing the ester thus formed with barium hydroxide; the acid crystallises in six-sided prisms and changes colour at 235° and finally melts and decomposes at 273—274°; it resembles tropic acid closely, but is less soluble in water; it is not oxidised by acid permanganate, but readily by alkaline permanganate and silver oxide. Its vapour colours a pine splinter moistened with hydrochloric acid intensely red. Measurements of the electrical conductivity show that even at high concentrations it behaves as a dibasic acid, whereas tropic acid behaves as a monobasic acid and has  $\kappa$  0·0426. The *copper* salt,  $C_7H_{10}O_4NCu \cdot OH \cdot 5H_2O$ , crystallises in pale blue leaflets; when dried at 105°,  $1H_2O$  is still retained; it melts and decomposes at 240°. The *silver* salt crystallises in slender needles. The *hydrochloride* forms six-sided prisms or plates which become coloured at 235°, decompose at 261—262° and are hydrolysed by water; the *platini-chloride* forms six-sided prisms. *Methyl 1-methylpyrrolidine-2:5-dicarboxylate* crystallises in long needles, melts at 35—36°, and boils at 140° under 17—18 mm. pressure; the *methiodide* of the ester crystallises in prisms decomposing at 120—120·5°.

1-Methylpyrrolidine 2:3:4:5-tetracarboxymethylamide,



is obtained by heating an alcoholic solution of ethyl  $\alpha\delta$ -dibromobutane-tetracarboxylate and methylamine for 10 hours; it forms colourless, four-sided prisms melting at 230—230·5°. On hydrolysis with barium hydroxide, a methylpyrrolidinedicarboxylic acid is formed which melts at 280—281° and is far less soluble than its isomeride.

*Methyl 1-methylpiperidine-2:6-dicarboxylate* is prepared by heating ethyl dibromopentane-tetracarboxylate (b. p. 251—253° under 12 mm. pressure) with a benzene solution of methylamine under pressure at 140—150°; the product is boiled with concentrated barium hydroxide, and the dicarboxylic acid thus obtained converted into its methyl ester; this ester is a colourless oil boiling at 140—141° under 13 mm. pressure. The *methiodide* crystallises in monoclinic prisms melting at 167—168°.

K. J. P. O.

**Phenolic Urethanes of Piperidine.** By BOUCHETAL DE LA ROCHE (*Bull. Soc. Chim.*, 1902, [iii], 27, 451—453).—Employing Cazeuue and Moreau's method (Abstr., 1899, i, 132), the author has prepared the following urethanes of piperidine. *o*-Chlorophenyl piperidinecarbamate,  $C_5H_{10}N \cdot CO \cdot O \cdot C_6H_4Cl$ , crystallises in colourless octahedra melting at  $119^\circ$  and boiling at  $148$ — $149^\circ$  under 273 mm. pressure; it is insoluble in water but soluble in alcohol. *p*-Chlorophenyl piperidinecarbamate is a yellow, crystalline substance which melts at  $65^\circ$  and boils at  $218$ — $219^\circ$  under 23 mm., and at  $284$ — $285^\circ$  under atmospheric pressure, at the same time rapidly undergoing decomposition; it is soluble in water, ether, carbon disulphide, acetone, or chloroform, and very soluble in hot alcohol. *Pentachlorophenyl piperidinecarbamate* forms lustrous, white crystals, melts at  $123^\circ$ , and boils at  $259^\circ$  under 11 mm. pressure; it is sparingly soluble in hot alcohol but fairly so in benzene. *o*-Tolyl piperidinecarbamate crystallises in white prisms and is very soluble in organic solvents; it melts at  $32^\circ$  and boils at  $193^\circ$  under 17 mm. pressure, and with decomposition at  $310^\circ$  under atmospheric pressure. *m*-Tolyl piperidinecarbamate melts at  $64^\circ$ , boils at  $195^\circ$  under 10.7 mm. pressure, and is soluble in alcohol, chloroform, ether, or acetone. *p*-Tolyl piperidinecarbamate forms white needles melting at  $85^\circ$  and boiling at  $201^\circ$  under 15 mm. pressure and at  $320^\circ$  under atmospheric pressure, undergoing at the same time slight decomposition. *Eugenyl piperidinecarbamate* crystallises in white plates which melt at  $93.5$ — $94^\circ$  and boil at  $239^\circ$  under 18 mm. pressure. *Thymyl piperidinecarbamate* has only been obtained as a yellow liquid boiling in a vacuum at  $204$ — $206^\circ$ .  
A. F.

**Relations of Hydrogen to Unsaturated Elements and Groups of Elements.** By DANIEL VORLÄNDER (*Ber.*, 1901, 35, 1845—1846).—The reactions of certain pyrrole derivatives which appear to Feist (this vol., i, 490) to be anomalous fall within the scope of the author's theory (Abstr., 1901, i, 444) and must therefore be considered normal.  
A. H.

**Furfuran and Pyrrole Groups.** By EDUARD A. KEHRER (*Ber.*, 1902, 35, 2009—2010).—In reply to Feist (this vol., i, 488), the author points out that 1:4-diketones may be readily obtained by the methods previously described (Abstr., 1899, i, 568; 1901, i, 389), and that on treatment with ammonia these diketones give good yields of pyrrole derivatives.  
J. J. S.

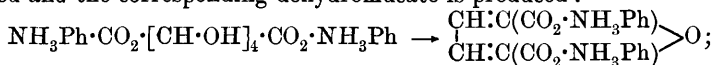
**Mechanism of the Formation of Pyrrole from the Salts of Mucic Acid.** By AMÉ PICTET and ALBERT STEINMANN (*Arch. Sci. phys. nat.*, 1902, [iv], 13, 342—351).—When normal aniline mucate is heated strongly, 1-phenylpyrrole is formed together with *s*-diphenylcarbamide. When heated at  $240^\circ$  for an hour, a residue is obtained from which 1-phenylpyrrole-2-carboxylic acid and 1-phenylpyrrole-2:5-dicarboxylic acid can be isolated.

1-Phenylpyrrole-2-carboxylic acid is obtained by dissolving the residue in alkali and precipitating with hydrogen chloride; when crystallised

from alcohol or benzene, it forms white needles which are odourless and tasteless and melt at  $166^{\circ}$ ; when fused, it decomposes into carbon dioxide and 1-phenylpyrrole. It is insoluble in cold water, and decomposed when boiled with water, but is easily soluble in alcohol, benzene, or chloroform, less so in acetic acid, sparingly in ether. Its alcoholic solution, to which hydrochloric acid has been added, imparts a violet coloration to a pine splinter immersed in it. The *ammonium*, *silver*, *copper*, and *calcium* salts have been prepared. The *methyl* ester boils at  $282^{\circ}$  without decomposition, forms colourless crystals which melt at  $88^{\circ}$ , and is very soluble in ether, benzene, chloroform, or acetic acid. The corresponding *ethyl* ester is a colourless liquid which boils at  $289^{\circ}$  and does not colour a pine splinter.

After extracting the monocarboxylic acid, crystals of 1-phenylpyrrole-2:5-dicarboxylic acid separate from the mother liquor. This substance has no definite melting point; at  $240^{\circ}$ , it decomposes into carbon dioxide and 1-phenylpyrrole; it is only sparingly soluble in cold water, chloroform, or benzene, but very easily in hot water, acetic acid, alcohol, or ether. It gives an insoluble silver salt.

On account of the formation of these two substances, the authors conclude that the formation of 1-phenylpyrrole from aniline mucate takes place in the following stages: (1) 3 mols. of water are eliminated and the corresponding dehydromucate is produced:



(2) 1 mol. of aniline is then split off, and this reacts with the oxygen in the ring with elimination of another mol. of water and formation of the aniline hydrogen salt of 1-phenylpyrrole-2:5-dicarboxylic acid; (3) the third phase is the splitting off of carbon dioxide with production of the aniline salt of 1-phenylpyrrole-2-carboxylic acid. The 1-phenylpyrrole is produced finally by the elimination of a mol. of aniline and one of carbon dioxide from the last salt. J. McC.

**Compounds of Silver Chloride with Organic Bases.** By CARL RENZ (*Ber.*, 1902, 35, 1954—1956).—Silver chloride dissolves in pyridine and in a solution of pyridine in hydrochloric acid, a double-salt being formed. This can be separated in crystalline form by evaporating the acid solution, and can be freed from pyridine hydrochloride by shaking with amyl alcohol. It has the formula  $\text{AgCl}_2(\text{C}_5\text{H}_5\text{N}, \text{HCl})$ , is unchanged by light, and permanent at the ordinary temperature, is soluble without decomposition in acetone, is not decomposed by amyl alcohol or benzene, but liberates silver chloride in contact with water, alcohol, ether, methyl alcohol, or glycerol.

The quinoline double salt,  $\text{AgCl}_2\text{C}_9\text{H}_7\text{N}, \text{HCl}$ , forms white needles, is permanent at the ordinary temperature, is not changed by light, and is decomposed by amyl alcohol as well as by water and alcohol, but can be purified by washing with ether. T. M. L.

**Condensation of Quinaldine with Cuminaldehyde and p-Tolualdehyde.** By FELIX VON GRABSKI (*Ber.*, 1902, 35, 1956—1958).—*Quinaldyl*-p-isopropyl- $\alpha$ -stilbazole,  $\text{C}_{20}\text{H}_{19}\text{N}$ , prepared by heating quinaldine with cuminaldehyde at  $180$ — $190^{\circ}$ , crystallises from alcohol

in colourless, thread-like needles and melts at 102°. The *hydrochloride*,  $C_{20}H_{19}N \cdot HCl$ , crystallises from dilute hydrochloric acid in small, yellow needles, sinters at 68°, and melts at 186°. The *platinichloride* forms yellow crystals and melts at 229—230°. The *mercurichloride* forms glistening, yellow needles and melts at 207—208°. The *picrate* forms dark yellow tablets and melts at 212°. The *dibromide*,  $C_{20}H_{19}NBr_2$ , crystallises from hot alcohol in colourless, glistening flakes and melts at 151°. The *stilbazoline*, prepared by reducing with sodium and alcohol, was obtained as a syrupy liquid; the *hydrochloride*,  $C_{20}H_{25}N \cdot HCl$ , crystallises in colourless, feathery needles.

*Quinaldyl-p-methyl- $\alpha$ -stilbazole*,  $C_{18}H_{15}N$ , prepared in a similar manner from quinaldine and *p*-tolualdehyde, crystallises from alcohol in long, yellow needles. The *hydrochloride* forms slender, yellow needles, sinters at 115° and melts at 218°. The *platinichloride*, *mercurichloride*, and *picrate* were also prepared and analysed. *Quinaldyl-p-methyl- $\alpha$ -stilbazoline*,  $C_{18}H_{21}N$ , is a thick oil, and boils at 249—250° under 25 mm. pressure. The *hydrochloride* forms pale yellow needles, sinters at 220°, and melts at 229°.

*Quinaldyl- $\alpha$ -stilbazoline*,  $C_{17}H_{19}N$ , prepared by reducing Wallach and Wüsten's benzylidenequinaldine (Abstr., 1883, 1096), is a thick, yellowish oil, and boils at 229—230° under 20 mm. pressure. The *hydrochloride* forms white needles, darkens in colour when heated and melts at 210—211°. The *benzoyl* derivative forms slender, silky needles and melts at 107°. T. M. L.

**Isomeric Change of Methyl Cinchomerone into Apophyllenic Acid.** By ALFRED KIRPAL (*Monatsh.*, 1902, 23, 239—249. Compare Abstr., 1901, i, 227).—Cinchomeronic acid is converted by sodium hypobromite into 4-aminonicotinic acid,  $C_5H_3N \begin{smallmatrix} \diagup CO \\ \diagdown NH_3 \end{smallmatrix} O$ , which crystallises from water in thick, colourless prisms or in delicate needles and decomposes at above 340°. The *sulphate*,  $(C_6H_6O_2N_2)_2 \cdot H_2SO_4$ , crystallises from dilute sulphuric acid in long, colourless needles, the *hydrochloride* forms delicate, glistening needles and decomposes at 270°, the *platinichloride* forms orange-coloured prisms and decomposes at 250°. When heated at 340°, the acid decomposes into carbon dioxide and 4-aminopyridine (m. p. 154°). When heated with methyl alcohol and hydrogen chloride, the acid forms its *methyl* ester which is easily soluble in hot chloroform or alcohol, melts at 173°, and is easily hydrolysed by alkalis or concentrated sulphuric acid, but with great difficulty by the dilute acid. 4-Aminonicotinic acid cannot be diazotised in dilute sulphuric acid solution; when diazotised in concentrated sulphuric acid and boiled, after addition of water, it is converted into 4-hydroxynicotinic acid which melts with evolution of gas at 250° and yields 4-hydroxypyridine (m. p. 66°).

When  $\gamma$ -methyl cinchomerone is heated at 154°, it is converted into apophyllenic acid, which crystallises from water in needles and melts at 240°. Apophyllenic acid must be isonicotinic-betaïne-3-carboxylic acid (compare Abstr., 1886, 369). G. Y.

**Cinchomeronic Acid and Apophyllenic Acid.** By KARL KAASS (*Monatsh.*, 1902, 23, 250—261).—Cinchomeronic acid is best purified

by recrystallisation of its hydrochloride.  $\alpha$ -Methyl cinchomerate, prepared by treatment of the anhydride with methyl alcohol, yields a violet, crystalline, copper salt (compare Abstr., 1900, i, 51).  $\beta$ -Methyl cinchomerate is formed by hydrolysis of dimethyl cinchomerate with cold alcoholic potassium hydroxide; it is a crystalline powder, soluble in methyl alcohol, melts at  $160^\circ$ , and yields a light blue, crystalline, copper salt which does not change its colour on warming.

When heated with methyl iodide at  $100^\circ$ ,  $\alpha$ -methyl cinchomerate yields apophyllenic acid and a *methiodide*,  $\text{CO}_2\text{H}\cdot\text{C}_5\text{NH}_3\cdot\text{CO}_2\text{Me}, \text{MeI}$ , which forms granular crystals and melts at  $223\text{--}224^\circ$ .  $\beta$ -Methyl cinchomerate forms a *methiodide* which melts at  $188^\circ$ , but not apophyllenic acid.

When heated at  $180^\circ$ ,  $\alpha$ -methyl cinchomerate yields cinchomeronic acid and apophyllenic acid.

Apophyllenic acid prepared from  $\alpha$ -methyl cinchomerate or from cotarnine melts at  $229\text{--}232^\circ$  (compare Kirpal, preceding abstract).

*Note.*—The ester termed  $\alpha$ -methyl by this author is the  $\gamma$ -methyl ester of Kirpal. G. Y.

**Hofmann's Reaction.** By ZDENKO H. SKRAUP and G. PICCOLI (*Monatsh.*, 1902, 23, 269—285. Compare Abstr., 1901, i, 226).—Diethyl methylhexahydrocinchomerate is a light yellow liquid, has a slight amine-like odour, boils at  $153\text{--}155^\circ$  under 26 mm. pressure and yields, with methyl iodide, a *methiodide* which crystallises in microscopic, triangular plates, is soluble in cold water or boiling alcohol, and melts at  $141^\circ$ . When treated with potassium hydroxide in concentrated aqueous solution, the *methiodide* yields an oil, which, when boiled with dilute alkali, is hydrolysed to an *acid* probably having the constitution  $\text{NMe}_2\cdot\text{CH}\begin{matrix} \text{CH}_2\cdot\text{CH}\cdot\text{CO}_2\text{H} \\ \text{CH}_2\cdot\text{CH}\cdot\text{CO}_2\text{H} \end{matrix}$  or  $\text{CH}_2\begin{matrix} \text{CH}_2\text{---CH}\cdot\text{CO}_2\text{H} \\ \text{CH}(\text{NMe}_2)\cdot\text{CH}\cdot\text{CO}_2\text{H} \end{matrix}$ . It forms a crystalline powder, is soluble in alcohol when slowly heated, becomes brown at  $245^\circ$ , and melts and decomposes at  $263^\circ$ . If introduced into a bath at  $230^\circ$  and rapidly heated, it melts at  $273^\circ$ . The *potassium* and *copper* salts are described. The *platinichloride* crystallises in long plates, sinters at  $235^\circ$ , and melts at  $239^\circ$ . The *aurichloride* melts at  $195^\circ$ . When fused with potassium hydroxide, diethyl methylhexahydrocinchomerate *methiodide* yields  $\alpha$ -methyltricarballic acid (Abstr., 1892, 41) and small quantities of oxalic acid. G. Y.

**Isomeric Dihydrolutidinedicarboxylic Esters of R. Schiff and P. Prosio.** By EMIL KNOEVENAGEL and J. FUCHS (*Ber.*, 1902, 35, 1788—1799).—Schiff and Prosio (Abstr., 1896, i, 250) stated that ethyl dihydrolutidinedicarboxylate (m. p.  $183\text{--}185^\circ$ ) was converted by concentrated hydrochloric acid into an isomeric ester melting at  $58\text{--}62^\circ$ . It is shown by the authors that this product is a mixture of ethyl lutidinedicarboxylate (2 mols.) and ethyl hexahydrolutidinedicarboxylate (1 mol.). From this mixture, the former ester can be separated in the form of the picrate. By the action of sodium nitrite on the mixture, the yellow *nitroso*-derivative of ethyl hexahydrolutidinedicarboxylate,  $\text{C}_{13}\text{H}_{22}\text{O}_5\text{N}_2$ , is obtained, melting at  $54^\circ$ ; on reduction, it yields ammonia and the original hexahydro-ester. By means of

light petroleum, the mixture (m. p. 58—62°) can be separated into ethyl lutidinedicarboxylate (m. p. 73°) which is readily soluble, and ethyl hexahydrolutidinedicarboxylate (m. p. 92—94°), which is insoluble. The last-mentioned substance crystallises in small, white cubes and is very readily oxidised by the air (taking up 2 atoms of oxygen and losing 1 mol. of water). The *platinichloride* melts and decomposes at 128°. The *platinichloride* of ethyl lutidinedicarboxylate forms golden yellow crystals melting at 197°.

K. J. P. O.

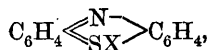
**Formation of Dinitrophenoxazines.** By J. C. CROCKER (*Proc. Camb. Phil. Soc.*, 1902, 11, 342—346).—The products of reaction of picryl chloride on some *o*-hydroxyamino-compounds have been examined.

In alcoholic solution, sodium amino- $\beta$ -naphtholsulphonate gives, with picryl chloride, bronze crystals of sodium naphthadinitrophenoxazine-sulphonate. *o*-Aminophenolsulphonic acid gives a rouge-coloured powder of sodium dinitrophenoxazinesulphonate, which is almost insoluble in alcohol or acetic acid.  $\alpha$ -Amino- $\beta$ -naphthol gives brown, silky needles of naphthadinitrophenoxazine which decompose at 274°. *o*-*p*-Diaminophenol gives dipicraminophenol in the form of dark-red plates which melt at 185°, are easily soluble in acetic acid or cold potassium hydroxide solution, but only sparingly so in alcohol. Dipicraminophenol gives, with acetyl chloride, dipicraminophenylacetate, which separates from dilute acetic acid in reddish-yellow plates melting at 223°. Dipicraminophenol is extremely soluble in aniline, and from the solution alcohol precipitates brown crystals which contain aniline and melt at 269°. After evaporation of the aniline and crystallisation from dilute acetic acid, a dark bronze powder of picraminodinitrophenoxazine is obtained melting at 277°. The aminophenol may also be condensed with sodium phosphate to form oxazine.

Aminothymol [ $\text{CH}_3 : \text{NH}_2 : \text{Pr} : \text{OH} = 1 : 2 : 4 : 5$ ] gives, with picryl chloride, a brownish powder of picraminothymol which melts at 212°.

J. McC.

**Constitution of the Oxazine and Thiazine Colouring Matters and their Relationship to the Azonium Compounds.** By FRIEDRICH KEHRMANN (*Annalen*, 1902, 322, 1—77. Compare Abstr., 1900, i, 62; 1901, i, 484; this vol., i, 186, 235, and Green, Abstr., 1900, i, 119).—In the light of recent investigations, oxazine and thiazine colouring matters must be regarded, not as *p*-quinone derivatives but as compounds of the *o*-quinone type; the parent substances of the two series having the formulæ  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \text{OX} \end{smallmatrix} \text{C}_6\text{H}_4$  and



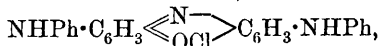
analogous with the azonium salts,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \text{NPhX} \end{smallmatrix} \text{C}_6\text{H}_4$ , where X is an acid radicle.

[With CARLO STAMPA.]—Although phenazoxone, obtained by oxidising phenoxazine is unstable, yet the products formed by carrying out this operation in the presence of amines are readily isolated. 3-*Anilino*phenazoxonium chloride,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \text{OCl} \end{smallmatrix} \begin{smallmatrix} \text{C} \cdot \text{CH} : \text{CH} \\ \text{C} \cdot \text{CH} : \text{C} \cdot \text{NHPh} \end{smallmatrix}$ , produced in



this way by the action of an alcoholic solution of ferric chloride and aniline hydrochloride, crystallises from this solvent in deep red, transparent leaflets and melts at 196—198°; the corresponding *nitrate* crystallises from hot water in dark red needles having a brass-like lustre.

3 : 9-*Dianilinophenazoxonium chloride*,

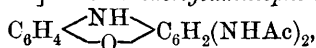


prepared by treating the preceding salt with aniline hydrochloride and aniline, separates from dilute alcohol in lustrous spangles with a golden reflex. On rendering the solution of this salt alkaline with sodium carbonate, the anhydro-base,  $\text{NPh} \begin{array}{c} \text{C}_6\text{H}_3 \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{C}_6\text{H}_3 \cdot \text{NPh}$ , is obtained as a green, crystalline powder.

A mixture of dimethylphenoxazines is produced by condensing 2-methylcatechol with 4-amino-*m*-cresol, one isomeride, probably 3 : 9-dimethylphenoxazine,  $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{C}_6\text{H}_3\text{Me}$ , crystallises from benzene in light grey plates melting at 204—205°; the other base has not yet been obtained pure. The former isomeride readily yields azoxonium salts on oxidation; *dimethylphenazoxonium picrate* is a violet, crystalline powder.

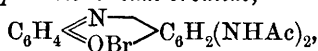
[With WALTER URECH.]—3-*Methylphenoxazine*, prepared from catechol and 4-amino-*m*-cresol, separates from light petroleum in colourless, granular crystals melting at 123—125°, and yields only a monanilino-oxonium compound on treatment with aniline and an oxidising agent.

[With PAUL THOMAS.]—3 : 5-*Diacetylaminophenoxazine*,



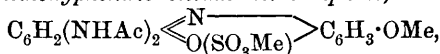
produced by warming the stannochloride of diaminophenoxazine (compare Abstr., 1900, i, 62, and Trans., 1891, 59, 714) with dry sodium acetate and acetic anhydride, crystallises from alcohol in pale greyish-yellow needles.

3 : 5-*Diacetylaminophenazoxonium bromide*,



prepared by treating an aqueous suspension of the preceding base successively with ferric chloride and sodium bromide, separates in small, steel-blue crystals; it is extremely reactive, being readily oxidised

to *diacetylaminophenazoxone*,  $\text{O} \begin{array}{c} \text{C}_6\text{H}_3 \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{O} = \end{array} \text{C}_6\text{H}_2(\text{NHAc})_2$ , a substance crystallising in small, brown needles melting at 110—120°. 3 : 5-*Di-acetylamino-9-methoxyphenazoxonium methosulphate*,



is obtained by treating the azoxone, dissolved in nitrobenzene, with dimethyl sulphate at 150—160°. 9-*Anilino-3 : 5-diacetylaminophen-*

*azoxonium anhydride*,  $\text{NPh} \begin{array}{c} \text{C}_6\text{H}_3 \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{O} = \end{array} \text{C}_6\text{H}_2(\text{NHAc})_2$ , produced either from the bromide or the methyl sulphate by the action of an alcoholic solution of aniline, crystallises from a mixture of this solvent with

benzene in dark red needles with a metallic lustre and melts at  $273^{\circ}$ .

3:5-Diaminophenazoxone,  $O \begin{smallmatrix} \diagup C_6H_3 \cdot N \\ \diagdown O = C_6H_2(NH_2)_2 \end{smallmatrix}$ , obtained by hydrolysing the corresponding diacetyl derivative with 50 per cent. sulphuric acid, crystallises from alcohol in long, green needles.

[With GEORG HERRMANN.]—Ethyl phenanthrazoxonium  $\psi$ -oxide,  $C_6H_4 \cdot C \begin{smallmatrix} \diagup N \\ \diagdown C_6H_4 \cdot C(OEt) \cdot O \end{smallmatrix} > C_{14}H_8$ , results from the action of alcohol and sodium carbonate on phenanthrazoxonium perbromide (Abstr., 1901, i, 484); it crystallises from alcohol or benzene in lustrous, yellow needles, melting first at  $245^{\circ}$  and subsequently at  $283^{\circ}$ .

Phenanthrazoxonium chloride,  $C_6H_4 \cdot C \begin{smallmatrix} \diagup N \\ \diagdown C_6H_4 \cdot C \cdot OCl \end{smallmatrix} > C_{14}H_8$ , prepared by adding excess of concentrated hydrochloric acid to an alcoholic solution of the preceding compound, separates, with  $3H_2O$ , as a crystalline powder with a coppery reflex; it is insoluble in water and decomposed on boiling with alcohol.

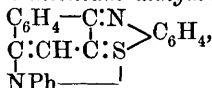
[With O. VESELY.] (Compare this vol., i, 186.)—3-Anilinophenazothionium chloride,  $NHPh \cdot C_6H_3 \begin{smallmatrix} \diagup N \\ \diagdown SCl \end{smallmatrix} > C_6H_4$ , produced by oxidising thiodiphenylamine with ferric chloride in the presence of aniline hydrochloride, separates in coppery needles; on treatment with alkaline solutions, it yields the anhydro-base,  $NPh \begin{smallmatrix} \diagup C_6H_3 \cdot N \\ \diagdown S - C_6H_4 \end{smallmatrix}$ , crystallising in dark red leaflets with a brass-like lustre and melting at  $150^{\circ}$ .

3:9-Dianilinophenazothionium chloride (diphenylthionine chloride), obtained by treating the preceding salt with aniline and alcohol, separates from this solvent in lustrous crystals.

Phenazothionium anhydro-3-sulphanilate,  $N \begin{smallmatrix} \diagup C_6H_3 \cdot NH \\ \diagdown C_6H_4 \cdot S \cdot O - SO_2 \end{smallmatrix} > C_6H_4$ , results from the oxidation of thiodiphenylamine in the presence of sodium sulphanilate; it separates as a greenish-black powder.

[With ALFRED GRESSLY and E. MISSLIN.]— $\alpha$ -Naphthaphenazothionium picrate,  $C_{10}H_6 \begin{smallmatrix} \diagup N \\ \diagdown S [O \cdot C_6H_2(NO_2)_3] \end{smallmatrix} > C_6H_4$ , prepared by oxidising thiophenyl- $\alpha$ -naphthylamine with ferric chloride in the presence of picric acid, separates in brown needles.

11-Anilino- $\alpha$ -naphthaphenazothionium anhydride,



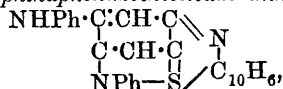
produced by oxidising thiophenyl- $\alpha$ -naphthylamine in the presence of aniline hydrochloride, crystallises from alcohol or benzene in lustrous, brownish-red leaflets melting at  $179^{\circ}$ . Boiling dilute mineral acids hydrolyse the substance with the formation of salts.

3-Anilino- $\beta$ -naphthaphenazothionium anhydride,  $\begin{array}{c} H : CH \cdot C \\ | \quad | \\ C = CH \cdot C \\ | \quad | \\ NPh - S \end{array} \begin{smallmatrix} \diagup N \\ \diagdown C_{10}H_6 \end{smallmatrix}$ ,

obtained from thiophenyl- $\beta$ -naphthylamine, crystallises from alcohol or benzene in lustrous, violet-brown leaflets melting at  $175^{\circ}$ ; mineral acids hydrolyse it, yielding salts.

$\beta$ -Naphthaphenazothionium picrate,  $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} \begin{smallmatrix} \text{O} \cdot C_6H_2(NO_2)_3 \end{smallmatrix} > C_6H_4$ , separates in small, green needles and dissolves in concentrated sulphuric acid to a violet-blue solution.

3:4-Dianilino- $\beta$ -naphthaphenazothionium anhydride,



produced by boiling the preceding anhydride with an alcoholic solution of aniline hydrochloride, crystallises from benzene or alcohol in reddish-brown needles with a metallic reflex and melts at  $229^{\circ}$ .

$\beta$ -Naphthazothionium picrate,  $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} \begin{smallmatrix} \text{O} \cdot C_6H_2(NO_2)_3 \end{smallmatrix} > C_{10}H_6$ , is obtained in small, dark-green needles by oxidising thio- $\beta$ -dinaphthylamine with ferric chloride in the presence of picric acid. It was not found possible to obtain anilino-derivatives of  $\beta$ -naphthazothionium hydroxide either by oxidising thio- $\beta$ -dinaphthylamine in the presence of aniline hydrochloride or by digesting the azothionium derivative with this salt.

Thio- $\alpha$ -dinaphthylamine, prepared by heating  $\alpha$ -dinaphthylamine with sulphur at  $230$ – $240^{\circ}$ , crystallises from alcohol in orange-yellow leaflets and melts at  $176$ – $177^{\circ}$ ; when oxidised, it gives rise to  $\alpha$ -dinaphthazothionium derivatives, the *picrate* forms deep violet needles, whilst the anilino-derivative is unstable and is readily hydro-

lysed to  $\alpha$ -dinaphthazothione,  $\begin{smallmatrix} C_6H_4 \cdot C : N \\ C : CH \cdot C : S \end{smallmatrix} > C_{10}H_6$ , a substance crystal-

lising from alcohol or benzene in dark brown leaflets melting at  $245^{\circ}$ .

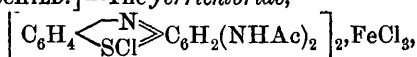
[With ANATOL DENGUIN.]—Phenazothione,  $\begin{smallmatrix} CH \cdot CH \cdot C : N \\ C = CH \cdot C : S \end{smallmatrix} > C_6H_4$ ,

formed by treating 3-aminophenazothionium chloride with sodium carbonate, is more readily prepared by oxidising thiodiphenylamine with a solution of ferric chloride in boiling dilute alcohol; it crystallises from benzene in reddish-brown leaflets and melts at  $165$ – $166^{\circ}$ .

Phenonaphthazothione,  $\begin{smallmatrix} C_6H_4 - C \\ | \quad \quad | \\ C : CH \cdot C \\ | \quad \quad | \\ O - S \quad C_6H_4 \end{smallmatrix} \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix}$  obtained by prolonged diges-

tion of a dilute solution of  $\alpha$ -naphthaphenazothionium sulphate at the ordinary temperature, separates from benzene in brownish-red crystals and melts at  $176^{\circ}$ .

[With LEO SCHILD.]—The *ferrichloride*,



produced by adding excess of ferric chloride to an alcoholic solution

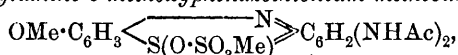
of 3:5-diacetylaminothiodiphenylamine, is a dark green, crystalline precipitate, which readily gives rise to 3:5-diacetylaminophenazothione,  $\text{O} \left\langle \begin{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{N} \\ \text{S} = \text{C}_6\text{H}_2(\text{NHAc})_2 \end{smallmatrix} \right\rangle$ , a substance separating in dark brown needles. This azothione readily undergoes hydrolysis, yielding 3:5-diaminophenazothione.

9-Anilino-3:5-diacetylaminophenazothionium chloride results from the action of aniline hydrochloride on the double ferric salt, and separates from alcohol or benzene in lustrous, granular crystals; the anhydride,

$\text{NPh} \left\langle \begin{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{N} \\ \text{S} = \text{C}_6\text{H}_2(\text{NHAc})_2 \end{smallmatrix} \right\rangle$ , set free by ammonium carbonate crystallises from alcohol in reddish-brown needles and melts at 220—225°.

9-Anilino-3:5-diaminophenazothionium chloride separates in green granules with a metallic lustre on boiling the preceding anhydride with alcoholic hydrochloric acid; it is not affected by ammonia or alkali carbonates, but is decomposed by sodium hydroxide.

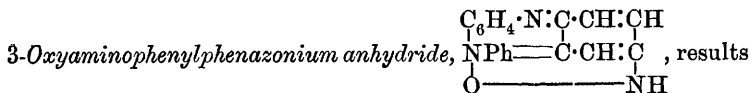
3:5-Diacetylamino-9-methoxyphenazothionium methosulphate,



produced by the action of dimethyl sulphate on 3:5-diacetylaminophenazothione in nitrobenzene solution at 150°, is a brown powder which yields the corresponding dichromate,  $(\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_8\text{S})_2\text{Cr}_2\text{O}_7$ , by double decomposition with potassium dichromate; the sulphate is reconverted into 9-anilino-3:5-diacetylaminophenazothionium chloride by the successive action of aniline and hydrochloric acid.

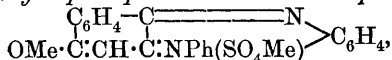
[With VICTOR VESELÝ.]—Resorcinolazodiphenyl aminesulphoxide,  $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{NH} \\ \text{SO} \end{smallmatrix} \right\rangle \text{C}_6\text{H}_3 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{OH})_2$ , results from the action of diazotised 3-aminophenazothionium chloride on an aqueous solution of resorcinol containing sodium acetate; it crystallises from alcohol or benzene in reddish-yellow needles; a sparingly soluble bye-product separates out first from this mixture of solvents, which is probably a diazo-compound. The azo-derivative is insoluble in water, but on the addition of sodium hydroxide dissolves to a deep red solution; it develops a green coloration with concentrated sulphuric acid, this change being probably due to the formation of an unstable sulphate.

[With HANS BECKER and ALEXANDER CAPATINA.]—Phenyldihydrophenazine,  $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{NH} \\ \text{NPh} \end{smallmatrix} \right\rangle \text{C}_6\text{H}_4$ , is prepared by reducing the phenylphenazonium ferrichloride obtained from picrylphenyl-*o*-phenylenediamine (Abstr., 1901, i, 52) with stannous chloride in dilute alcoholic solution; it crystallises from benzene in greyish-yellow leaflets, melts at 143°, and rapidly oxidises on exposure to the air, giving rise to aposaffranone (m. p. 248—249°); other oxidising agents produce the same effect. When only half the theoretical amount of reducing agent is employed in the preceding experiment, the solution assumes a green colour and contains an intermediate compound of the quinhydrone type which may be precipitated by sodium chloride and crystallised from alcohol in dark green prisms.



from the action of hydroxylamine hydrochloride and sodium acetate on phenylphenazonium stannichloride dissolved in dilute alcohol; it separates from benzene or alcohol in dark red crystals, dissolves in glacial acetic acid, and develops a green coloration with concentrated sulphuric acid (compare Abstr., 1899, i, 82, and Fischer and Hepp, Abstr., 1901, i, 463).

11-Methoxy-1-phenylnaphthaphenazonium methosulphate,



is readily obtained by adding methyl sulphate to a nitrobenzene solution of rosindone at 150° and diluting the product with ether; it crystallises in orange-yellow needles; the corresponding *bromide*, prepared by double decomposition, separates in golden-yellow leaflets soluble in water or alcohol. The *platinichloride* precipitated from an aqueous solution of the methyl sulphate on the addition of chloroplatinic acid forms brick-red crystals, developing with concentrated sulphuric acid a purple coloration. The bromide, when treated with an alcoholic solution of ammonia or aniline, gives rise to rosinduline or phenylosinduline respectively, the former being identical with the product of the action of 4-amino- $\beta$ -naphthaquinone on phenyl-*o*-phenylene hydrochloride.

G. T. M.

**Nitrosoacylphenylhydrazines.** By HUGO VOSWINCKEL (*Ber.*, 1902, 35, 1943—1947).—Nitrosobenzoylphenylhydrazine dissolves in dilute aqueous sodium hydroxide, but on adding an excess of the alkali, crystals of the *sodium* derivative,  $\text{NO}\cdot\text{NPh}\cdot\text{NNa}\cdot\text{COPh}$ , separate; this can be recrystallised from acetone, and by methyl iodide is converted into *o*-nitroso- $\beta$ -benzoyl- $\alpha$ -phenyl- $\beta$ -methylhydrazine,  $\text{NO}\cdot\text{NPh}\cdot\text{NMe}\cdot\text{COPh}$ , which forms stout, yellowish prisms, melts at 108°, and is reduced in alcoholic solution by stannous chloride and hydrochloric acid to  $\beta$ -benzoyl- $\alpha$ -phenyl- $\beta$ -methylhydrazine,  $\text{NHPh}\cdot\text{NMe}\cdot\text{COPh}$ . The latter crystallises from dilute alcohol, melts at 136°, and is converted by benzoyl chloride into  $\alpha\beta$ -dibenzoyl- $\alpha$ -phenyl- $\beta$ -methylhydrazine (Tafel, Abstr., 1885, 1060), a fact which proves its structure.

The *silver* derivative,  $\text{NO}\cdot\text{NPh}\cdot\text{NAg}\cdot\text{COPh}$ , corresponding with the foregoing sodium compound, is unstable and decomposes almost immediately after being precipitated; an attempt to replace the metal by alkyl groups gave only benzoylazobenzene,  $\text{NPh}:\text{N}\cdot\text{COPh}$ , which is converted by concentrated hydrochloric acid into benzoyl-*o*-chlorophenylhydrazine,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{NH}\cdot\text{COPh}$  (Hantzsch and Singer, Abstr., 1897, i, 216).

1-Phenylbenzothiazole is formed on fusing benzoylphenylhydrazine with sulphur.

W. A. D.

**Additive Compounds of Aldehydes with Phenylhydrazine-*p*-Sulphonic Acid.** By HEINRICH BILTZ, A. MAUÉ, and FR. SIEDEN (*Ber.*, 1902, 35, 2000—2008).—Phenylhydrazine-*p*-sulphonic acid combines with a number of aldehydes forming somewhat unstable additive compounds of the type  $\text{OH}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ ,

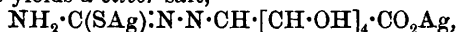
which can often be obtained in a crystalline form by the addition of the aldehyde to the sulphonic acid in the presence of a small amount of water. They are mostly yellow compounds, soluble in water and somewhat readily decomposed by water, especially when boiled. Decomposition occurs more readily when the compounds are boiled with dilute acids. The sodium salts are colourless or pale yellow, and may be crystallised from warm water. The formation of substituted phenylhydrazones by the elimination of water has not been observed.

The stability of the compounds increases with the presence of negative groups, for example, nitro- and hydroxyl groups, in the aldehyde molecule; whereas positive groups, for example, aryl groups, tend to diminish the stability.

*Benzaldehydephenylhydrazone-p-sulphonic acid hydrate* decomposes at about 95°. The compound from salicylaldehyde decomposes at about 110°; that from anisaldehyde sinters at 120° and melts and decomposes at 155—165°. *m-Nitrobenzaldehydephenylhydrazone-p-sulphonic acid hydrate* decomposes between 80° and 90°. The compounds with cinnamaldehyde, cinnamaldehyde, and valeraldehyde are so unstable that they could not be obtained pure. J. J. S.

**Method of Isolating Aldehydes and Ketones.** By CARL NEUBERG and W. NEIMANN (*Ber.*, 1902, 35, 2049—2056).—The thiosemicarbazones of aldehydes and ketones readily yield insoluble copper, silver, and mercury derivatives, which can be used for the purpose of isolating these compounds. These salts are formed when alcoholic solutions of a salt of the metals and a thiosemicarbazone are mixed; the copper and silver salts are amorphous, whilst the mercury salts are crystalline.

*Valeraldehydethiosemicarbazone*,  $C_4H_9 \cdot CH \cdot N \cdot NH \cdot CS \cdot NH_2$ , prepared by adding a concentrated aqueous solution of thiosemicarbazide to an alcoholic solution of valeraldehyde, is crystalline and melts at 65°; the *silver* salt is obtained as an amorphous powder when an alcoholic solution of silver nitrate is added to an alcoholic solution of the thiosemicarbazone. *isoValeraldehydethiosemicarbazone* melts at 52—53° and gives a *silver* salt. *Heptaldehydethiosemicarbazone* forms crystals and yields a *silver* salt. *Acetophenonethiosemicarbazone*, melts at 108° and yields a *silver* salt. *Piperonalthiosemicarbazone* melts at 185° and becomes rose-coloured in the air; the *silver* salt is a very stable powder. *Citronellalthiosemicarbazone* melts at 54—55°, and *menthone-thiosemicarbazone* crystallises in needles melting at 155—157°. *Glyoxaldithiosemicarbazone* is obtained from glyoxal and thiosemicarbazide, or less easily from trichlorolactic acid and the semicarbazide; it crystallises in yellowish needles decomposing above 300°, is soluble in dilute alkalis or alkali carbonates, and forms a yellowish-green, amorphous *silver* salt. The *thiosemicarbazone* of *d*-dextrose crystallises in rhombic plates melting at 204°, that of *d*-mannose melts at 187°, and that of *d*-galactose at 148°; the latter crystallises in long needles. The thiosemicarbazones of the sugars do not yield silver salts. *d*-Glucuronthiosemicarbazone yields a *silver* salt,



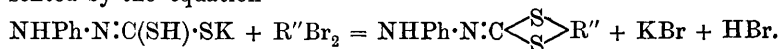
the lactone ring being opened.

The thiosemicarbazones are readily obtained from the silver salts by decomposing them with hydrogen sulphide in the presence of alcohol or ether; the aldehyde or ketone can be recovered from the thiosemicarbazone by the action of mineral acids or by heating them with phthalic anhydride.

The view is expressed that in these salts the metallic atom is attached to the sulphur atom.

K. J. P. O.

**Limits of the Formation of Cyclic Dithiocarbonates.** By MAX BUSCH and EDMUND LINGENBRINK (*J. pr. Chem.*, 1902, [ii], 65, 473—479).—In certain cases (Abstr., 1900, i, 66, 411), it has been shown that a dithiocarbazinate reacts with a dihaloid to form the hydrazone of a cyclic dithiocarbonate. Potassium dithiocarbazinate is now shown to react in this way with trimethylene or *o*-xylylene dibromide, as well as with ethylene dibromide; a ring is formed containing six, seven, or five atoms respectively, and the reaction is represented by the equation



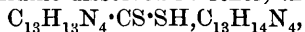
In the case of methylene and pentamethylene dibromides, where a similar reaction would result in the formation of rings containing four and eight atoms respectively, quite a different reaction occurs; the dithiocarbazinate reacts in the tautomeric form, yielding an ester which differs from the cyclic compounds in possessing acid properties; the equation is  $2\text{NHPh}\cdot\text{NH}\cdot\text{CS}_2\text{K} + \text{R}''\text{Br}_2 = (\text{NHPh}\cdot\text{NH}\cdot\text{CS}_2)_2\text{R}'' + 2\text{KBr}$ . In all cases, the reaction was allowed to take place in dilute alcoholic solution at the ordinary temperature.

Of the *phenylhydrazones* of cyclic dithiocarbonates, the *trimethylene*,  $[\text{R}'' = \text{CH}_2(\text{CH}_2)_2]$ , and *o*-xylylene,  $[\text{R}'' = \text{C}_6\text{H}_4(\text{CH}_2)_2]$ , derivatives melt at 76° and 202° respectively; the melting point of the ethylene derivative,  $[\text{R}'' = \text{CH}_2\cdot\text{CH}_2]$ , is now found to be 92°, not 94° (Abstr., 1894, i, 625) or 88° (Miolati, Abstr., 1891, 895).

*Methylene phenyldithiocarbazinate*,  $(\text{R}'' = \text{CH}_2)$ , melts at 167°; when boiled with aqueous formaldehyde, it condenses (compare Abstr., 1899, i, 825, 950) to the methylene ester of *phenylthiodiazolinethiol*,  $(\text{NPh}\cdot\text{N} \begin{array}{c} \text{---} \\ \diagup \quad \diagdown \\ \text{CH}_2\text{---S} \end{array} \text{C}\cdot\text{S})_2\text{CH}_2$ , which melts at 123—124°. *Pentamethylene phenyldithiocarbazinate*,  $[\text{R}'' = \text{CH}_2(\text{CH}_2\cdot\text{CH}_2)_2]$ , melts at 140—141°.

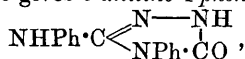
C. F. B.

**Aminoguanidines.** By MAX BUSCH and TH. ULMER (*Ber.*, 1902, 35, 1716—1726).—The *acid oxalate*,  $\text{C}_{13}\text{H}_{14}\text{N}_4\cdot\text{C}_2\text{H}_2\text{O}_4$ , obtained by mixing ethereal solutions of aminodiphenylguanidine and oxalic acid, melts and decomposes at 147°; when crystallised from alcohol, it is converted into the normal salt, and when heated alone at 160° it yields, by loss of water and carbon dioxide, 5-anilino-4-phenyltriazole (Busch and Bauer, Abstr., 1900, i, 414). On adding carbon disulphide to aminodiphenylguanidine dissolved in ether, the *salt*,



of the corresponding dithiocarbazinic acid is obtained as a yellowish-

white, crystalline powder. With phosgene dissolved in toluene, aminodiphenylguanidine gives 3-anilino-4-phenyl-5-triazolone,

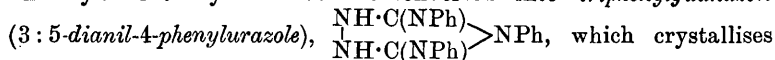


which crystallises from dilute alcohol in long, colourless needles and melts at 212—213°; with benzil, the *hydrazone*,



is obtained in the form of small, yellow prisms melting at 163—164°.

When aminodiphenylguanidine is heated at 180°, it loses aniline and hydrazine hydrate and is converted into *triphenylguanazole*



from alcohol in large leaflets with  $2\text{C}_6\text{H}_6\text{O}$ , melts at 234°, yields a crystalline *hydrochloride*,  $\text{C}_{20}\text{H}_{17}\text{N}_5\text{HCl}$ , melting at 127°, and is oxidised by alcoholic mercuric oxide, bromine water, or potassium

permanganate, to the *azo-compound*,  $\begin{array}{c} \text{N} \cdot \text{C}(\text{NPh}) \\ \text{N} \cdot \text{C}(\text{NPh}) \end{array} > \text{NPh}$ ; this forms blackish-brown, slender needles and melts at 192°. *Dimethyltriphenyl-*

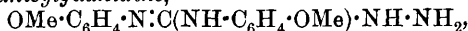
*guanazole*,  $\begin{array}{c} \text{NMe} \cdot \text{C}(\text{NPh}) \\ \text{NMe} \cdot \text{C}(\text{NPh}) \end{array} > \text{NPh}$ , obtained by methylating the base,

crystallises from alcohol in sheaves of prisms and melts at 182°; the analogous *diethyl* compound melts at 159—160°; *diacetyltriphenyl-guanazole* separates from glacial acetic acid in aggregates of stout prisms and melts at 218°.

*Tetraphenylhydrazodicarbonamidine*,  $\text{N}_2\text{H}_2[\text{C}(\text{NPh}) \cdot \text{NPh}]_2$ , is no doubt the intermediate product formed from aminodiphenylguanidine in the production of triphenylguanazole, as it is converted into the latter by loss of aniline when heated alone at 200° or when boiled with concentrated hydrochloric acid; it is best obtained by adding carbodiphenylimide in benzene solution to aminodiphenylguanidine or to hydrazine hydrate, and crystallises from alcohol in silky, efflorescent needles melting at about 164—165°.

*Tri-p-tolylguanazole* (3:5-ditolyl-4-tolylurazole), obtained by heating *aminodi-p-tolylguanidine* at 200°, crystallises from alcohol in colourless leaflets, melts at 223—224°, and forms a *hydrochloride*,  $\text{C}_{23}\text{H}_{23}\text{N}_5\text{HCl}$ , melting at about 105°; the *diacetyl* compound,  $\text{C}_{27}\text{H}_{29}\text{O}_2\text{N}_5$ , is granular and melts at 175°. Nitrous acid converts the *guanazole* dissolved in alcohol into *tri-p-tolyldehydroguanazole*,  $\begin{array}{c} \text{N} \cdot \text{C}(\text{N} \cdot \text{C}_7\text{H}_7) \\ \text{N} \cdot \text{C}(\text{N} \cdot \text{C}_7\text{H}_7) \end{array} > \text{N} \cdot \text{C}_7\text{H}_7$ , which crystallises in violet-blue needles, melts at 178°, and is also obtained by the action of bromine water or permanganate on the *guanazole*; it is reconverted into the latter by hydrogen sulphide.

*Aminodi-o-anisylguanidine*,



obtained by heating dianisylthiocarbamide with hydrazine hydrate and alcoholic potassium hydroxide for 4 hours at about 100°, is a syrup which yields a crystalline *picrate* melting at 154°. *Aminodi-β-naphthylguanidine*, prepared from di-β-naphthylcarbamide, crystallises from alcohol or benzene in needles, melts at 163—164°, and yields a



*hydrochloride*,  $C_{21}H_{18}N_4 \cdot HCl \cdot H_2O$ , melting at  $145^\circ$ ; the *nitrate* melts at  $95-96^\circ$ , and the *picrate* at  $196-197^\circ$  with decomposition. *Tri- $\beta$ -naphthylguanazole* crystallises from alcohol in soft needles and melts at  $216^\circ$ . W. A. D.

**Products of the Interaction of Hydrazine with Thiocarbamides. II.** By MAX BUSCH and TH. ULMER (*Ber.*, 1902, 35, 1710—1716).—When thiocarbanilide is heated with hydrazine hydrate and only a small proportion of alcoholic potash for four hours at  $130-135^\circ$ , 4-phenyl-5-aniltriazone-3-thiol,  $NPh \cdot C \begin{smallmatrix} \text{NH-N} \\ | \\ NPh \cdot C \cdot SH \end{smallmatrix}$ , is the principal product instead of aminodiphenylguanidine (*Abstr.*, 1900, i, 414); it is formed from the latter by the action of thiocarbanilide, thiocarbanilinoaminodiphenylguanidine being produced as an intermediate product, and can also be obtained by the interaction of aminodiphenylguanidine and phenylthiocarbimide. It crystallises from alcohol in sheaves of colourless prisms and melts at  $206^\circ$ ; the *potassium* salt forms colourless leaflets melting at  $125-126^\circ$ , and the *methyl* and *ethyl ethers* long needles melting at  $226-227^\circ$  and  $214-215^\circ$  respectively. 4-Phenyl-5-aniltriazone-3-disulphide,  $C_{28}H_{22}N_8S_2$ , obtained by oxidising the thiol with hydrogen peroxide or iodine, crystallises from alcohol in yellow needles and melts at  $209-210^\circ$ . If the potassium salt of the thiol be oxidised with alkaline hydrogen peroxide, 5-anilino-5-phenyltriazone (*loc. cit.*) is obtained.

In alcoholic solution in absence of alkali, diarylthiocarbamides of the type  $NHR \cdot CS \cdot NPh$  with hydrazine hydrate yield exclusively arylsemicarbazides, but a similar law does not hold for mixed aliphatic aromatic thiocarbamides.

4-p-Tolylthiosemicarbazide,  $C_7H_7 \cdot NH \cdot CS \cdot NH \cdot NH_2$ , crystallises from benzene in silvery leaflets melting at  $134-135^\circ$  and 4-anisylthiosemicarbazide in large leaflets melting at  $144^\circ$ . 4-p-Chlorophenylthiosemicarbazide melts at  $180^\circ$  and 4- $\alpha$ -naphthylthiosemicarbazide at  $138-139^\circ$ .

Phenylethylthiocarbamide is not attacked by alcoholic hydrazine hydrate at  $100^\circ$ . Attempts to prepare aminoguanidines from dibenzoyl thiocarbamide or diphenylbenzylthiocarbamide by the action of alcoholic hydrazine hydrate and potassium hydroxide at  $130-135^\circ$  also gave negative results. W. A. D.

**New Decompositions of the Diazo-compounds.** By JOACHIM BIEHRINGER and ALBERT BUSCH (*Ber.*, 1902, 35, 1964—1976).—The principal product of the action of copper powder on a mixture of benzenediazonium chloride and benzoyl chloride is dibenzoylhydrazobenzene,  $COPh \cdot NPh \cdot NPh \cdot COPh$ ; this, which was also prepared synthetically from hydrazobenzene, crystallises from alcohol in prisms or in pearly plates and melts at  $161^\circ$ . The isomeric dibenzoylbenzidine crystallises from nitrobenzene or from phenol in colourless prisms and melts at  $352^\circ$ . Dibenzoyldiphenylene, another isomeride, crystallises from nitrobenzene in microscopic forms and melts at  $277^\circ$ .

Monobenzoyl-o-aminodiphenylamine separates from wood spirit in colourless, monoclinic prisms. Dibenzoyl-p-aminodiphenylamine crys-

tallises from wood-spirit in rectangular tablets and melts at  $203^{\circ}$  (uncorr.).

*Dibenzoyl-p-hydrazotoluene*,  $C_{28}H_{24}O_2N_2$ , prepared by two similar methods, crystallises from light petroleum in colourless, silky plates and melts at  $157^{\circ}$ .

*Dibenzoyl-o-hydrazotoluene* crystallises from much hot water in colourless needles and melts at  $144^{\circ}$  (uncorr.). The isomeric *dibenzoyl-o-tolidine* is insoluble in most solvents except the organic bases, from which it separates on adding alcohol in colourless, microscopic needles melting at  $265^{\circ}$ .

T. M. L.

**Coupling of Toluidines with Diazo-compounds.** By HANS MEHNER (*J. pr. Chem.*, 1902, [ii], 65, 401—472).—Many examples were found of the long known fact that the same diazoamino-compound,  $X \cdot N_3 \cdot H \cdot Y$ , is obtained, whether  $X \cdot N_2 \cdot Cl$  and  $Y \cdot NH_2$ , or  $Y \cdot N_2 \cdot Cl$  and  $X \cdot NH_2$ , be the diazo-chloride and amine which are coupled. Further, in the coupling of *p*- and *m*-diazotoluene with aniline and of *p*-diazotoluene and *p*- and *m*-nitrodiazobenzene with *p*-toluidine, that is, in cases where the amine to be coupled is either aniline or a para-substituted aniline, only a diazoamino-compound is obtained. In other cases, a mixture is obtained of diazoamino- with aminoazo-compound in varying proportions. The presence of hydrogen ions appears to accelerate the transformation of diazoamino- into aminoazo-compound, for a larger yield of the former is obtained if sodium hydrogen carbonate instead of sodium acetate is added to the mixture of diazo-chloride and amine hydrochloride, and the yield is still larger if the solid diazo-salt is added to a cooled solution of the amine in pyridine and the product finally precipitated with ice and water. The last method was particularly efficacious when the amine was *m*-toluidine; in coupling this in pyridine solution with diazobenzene salt, the yield of diazoamino-compound was 90 per cent. of the whole, whereas it was only 40 per cent. when the coupling was effected in aqueous solution and sodium acetate was added. The use of sodium hydrogen carbonate has a disadvantage in cases where the amine only reacts slowly with the diazo-salt, for then the amine is largely thrown out of solution, and before all the diazo-salt has reacted with the amine some of it usually decomposes to a phenol which then couples with more of the diazo-salt to an hydroxyazo-compound. In this operation, a migration of the diazo-group from one radicle to the other must often occur, for only on this supposition is it possible to account for the constitution of the hydroxyazo-derivatives that are formed. In order to find the structure of the diazoamino-compounds,  $X \cdot N \cdot N \cdot NH \cdot Y$  (compare Goldschmidt, *Abstr.*, 1888, 685, 1283), additive products of these with phenylcarbimide,  $NHPh \cdot CO \cdot NY \cdot N \cdot NX$ , were prepared in ethereal solution, and these carbimide derivatives were hydrolysed by boiling their solutions in alcohol or 10 per cent. sulphuric acid, whereby a carbamide,  $NHPh \cdot CO \cdot NHY$ , is obtained. From the constitution of this carbamide, that of the original diazoamino-compound is inferred; it would have been  $Y \cdot N \cdot N \cdot NH \cdot X$  had the carbamide  $NHPh \cdot CO \cdot NHX$  been obtained. The two isomeric *p*-nitrobenzenediazoamino-*p*-toluenes (Bamberger, *Abstr.*, 1895, i, 351)

were examined, and the superior stability of the red modification is attributed to the fact that its crystals are larger than those of the yellow modification, and consequently have a relatively smaller surface and smaller solubility. A similar case of isomerism was discovered in the case of *p*-nitrobenzenediazoamino-*o*-toluene.

Hydroxyazo-compounds were formed in the following cases. *p*-Hydroxyazobenzene from diazobenzene with *o*-toluidine. 4-Hydroxy-3:2'-dimethylazobenzene, 4-hydroxy-2:2':2''-trimethyl-1:5-disazobenzene,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Me}(\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me})_2$ , and 4-hydroxy-3:4'-dimethylazobenzene (migration) from *o*-diazotoluene and *p*-toluidine. 4'-Nitro-2-hydroxy-5-methylazobenzene (migration), melting at  $186\cdot5^\circ$ , from *p*-nitrodiazobenzene and *p*-toluidine. 4'-Nitro 4-hydroxy-3-methylazobenzene (migration) from *p*-nitrodiazobenzene and *o*-toluidine.

The following are the other new compounds prepared, with their melting points. *Benzenediazoamino-m-toluene*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{N}\cdot\text{NHPh}$ ,  $86^\circ$ ; additive carbamide,  $116^\circ$ . *Benzeneazotoluenes*: *m*:*m*,  $76^\circ$ ; *o*:*m*,  $118-119^\circ$ ; *Diazoaminotoluenes*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ :—*m*:*p*,  $96-97^\circ$ ; additive carbamide,  $115^\circ$ ; *o*:*p*,  $119-120^\circ$ ; additive carbamide,  $117-118^\circ$  (phenyl-*o*-tolylcarbamide melts at  $196^\circ$ , not  $212^\circ$ ); contrary to the usual rule, the phenylcarbimide has added itself to the less negative radicle; *m*:*m*,  $50-52^\circ$ ; *o*:*m*,  $74^\circ$ ; additive carbamide, about  $117^\circ$ . 4-Amino-3:3'-dimethylazobenzene,  $124^\circ$ ; 4:2:2',  $116-117^\circ$ . *Nitrobenzenediazoaminotoluenes*:—*p*:*m*,  $138^\circ$ ; *p*:*o*,  $135^\circ$ ,  $139^\circ$ ; *m*:*m*,  $89-92^\circ$ ; *m*:*o*,  $110-111^\circ$ ; *o*:*p*,  $112\cdot5^\circ$ ; *o*:*m*,  $113-115^\circ$ ; *o*:*o*,  $134-135^\circ$ . *Nitroaminomethylazobenzenes*:—4':4:2,  $152-153^\circ$ ; 4':4:3,  $195-197^\circ$ ; 3':4:2,  $172^\circ$ ; 3':4:3,  $151-152^\circ$ ; 2':4:2,  $119-121^\circ$ ; 2':4:3,  $99^\circ$ .

C. F. B.

**A New System of Classification of Azo-dyes.** By HANS BUCHERER (*Chem. Centr.*, 1902, i, 917; from *Zeit. Farben. Textilchem.*, 1902, 1, 8—10, 45—46, 150—152).—The following system of indicating the composition of azo-dyes is not based on any scientific principle, but is devised simply for convenience of reference. The formula of azobenzene is written *b*·*b*, and in the case of substitution products the number of substituting groups in each benzene ring is shown by affixing a number thus, aminoazobenzene *b*·*b*<sub>1</sub>; aminoazobenzenesulphonic acid,  $\text{SO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{NH}_2$ , *b*<sub>1</sub>·*b*<sub>1</sub>; aminoazobenzenedisulphonic acid,  $(\text{SO}_3\text{H})_2\cdot\text{C}_6\text{H}_3\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{NH}_2$ , *b*<sub>1</sub>·*b*<sub>2</sub>. The naphthalene ring or residue is indicated by *n*, and the diphenyl residue by *B*. The dye prepared from toluidine, salicylic acid, and aminonaphthalenesulphonic acid, for instance, is written *b*<sub>2</sub>·*B*<sub>2</sub>·*n*<sub>3</sub>. This system allows of the use of a great number of symbols, which, when arranged in accordance with mathematical principles, considerably simplifies the process of identifying any azo-dye. By way of example, the system has been applied to the dyes contained in Schultz and Julius' summary (3 *Auflage*, 1897).

E. W. W.

**Phenylazoacetaldoxime and Voswinckel's Triazan Derivatives.** By EUGEN BAMBERGER (*Ber.*, 1902, 35, 1896—1900. Compare Voswinckel, this vol., i, 321).—It is urged that phenylazoacetaldoxime has the formula  $\text{NOH}\cdot\text{CMe}\cdot\text{N}\cdot\text{NPh}$ , and is not a pseudo-acid of the

formula  $\text{NO} \cdot \text{CHMe} \cdot \text{N} : \text{NPh}$ ; it alters the ratio of distribution of ammonia between toluene and air in favour of the former and behaves altogether like benzaldoxime.

Its reduction product,  $\text{C}_8\text{H}_{11}\text{N}_3$ , is probably  $\text{NH} : \text{CMe} \cdot \text{NH} \cdot \text{NPh}$  or  $\text{NH}_2 \cdot \text{CMe} \cdot \text{N} \cdot \text{NPh}$ , and not  $\text{CHMe} < \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} > \text{NPh}$ , and all the compounds described by Voswinckel (*loc. cit.*) as derivatives of triazan can be better formulated as open-chain compounds not containing a triazine-group.

T. M. L.

**Derivatives of Phenyltriazan.** By ALFRED WOHL and HANS SCHIFF (*Ber.*, 1902, 35, 1900—1904).—*Acetylformylphenylbenzylidenetriazan*,  $\text{CHO} \cdot \text{NAc} \cdot \text{NPh} : \text{N} : \text{CHPh}$ , prepared by the action of acetyl chloride and acetic anhydride on formylphenylbenzylidenetriazan, crystallises from alcohol in brilliant, white needles and melts at  $125^\circ$ . *Acetylphenylbenzylidenetriazan*,  $\text{NHAc} \cdot \text{NPh} : \text{N} : \text{CHPh}$ , prepared by boiling the preceding compound with alcoholic potash, crystallises from 50 per cent. alcohol in white needles and melts and decomposes at  $162$ — $164^\circ$ . *Nitrosoacetylphenylhydrazine*,  $\text{NO} \cdot \text{NPh} \cdot \text{NHAc}$ , melts and decomposes at  $63^\circ$  and is readily soluble in alcohol; when reduced and then condensed with benzaldehyde, it gives the acetylphenylbenzylidenetriazan just described; the alcoholic solution of the reduction product can be evaporated under reduced pressure without decomposition, but is decomposed on adding water and extracting with ether.

T. M. L.

**Fatty Aromatic Aminoazo-compounds. II.** By BERNH. PRAGER (*Ber.*, 1901, 35, 1862—1866. Compare this vol., i, 64).—The compound,  $\text{C}_{20}\text{H}_{22}\text{O}_5\text{N}_4$ , which is formed by the union of *p*-nitrobenzaldehyde with ethyl benzenazomethylaminocrotonate, appears to be *ethyl δ-hydroxy-α-phenylazo-β-methylimino-δ-p-nitrophenylvalerate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{C}(\text{NMe}) \cdot \text{CH}(\text{CO}_2\text{Et}) \cdot \text{N} : \text{NPh}$ . When heated with dilute acetic acid alone, it loses methylamine, forming *ethyl α-phenylazo-δ-nitrophenylpentane δ-ol-β-one-carboxylate*,

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}(\text{CO}_2\text{Et}) \cdot \text{N} : \text{NPh}$ , which crystallises in stellate groups of faintly yellow needles, melting at  $147$ — $148^\circ$  (corr.). Alcoholic sulphuric acid converts both this compound and the original substance into *α-phenylazo-δ-p-nitrophenylpentane-β-one-αδ-olide*,  $\text{O} < \begin{smallmatrix} \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NO}_2) \cdot \text{CH}_2 \\ \text{CO} \text{---} \text{CH}(\text{N} : \text{NPh}) \end{smallmatrix} > \text{CO}$ , alcohol and methylamine being eliminated; this substance decomposes at about  $218^\circ$  (corr.) and has the properties of a lactone, since it is insoluble in alkalis in the cold but dissolves on being heated.

In agreement with the constitution which is here assigned to it, the compound  $\text{C}_{20}\text{H}_{22}\text{O}_5\text{N}_4$  yields 1 mol. of aniline on reduction, whilst there is no formation of *ethyl α-aminoacetoacetate*.

A. H.

**Fractional Precipitation of Proteids by Salts.** By JEAN EFFRONT (*Chem. Centr.*, 1902, i, 1113; from *Mon. Sci.*, [iv], 16, 241—254).—In spite of its disadvantages, the fractional precipitation of proteids

with salts like ammonium sulphate and zinc sulphate is recommended as trustworthy for their separation. W. D. H.

**Silk Glue—Sericin.** By S. BONDI (*Zeit. physiol. Chem.*, 1902, 34, 481—499. Compare Cramer, *J. pr. Chem.*, 1865, 96, 76; Bolley, *ibid.*, 1869, 108, 364).—The sericin was obtained by a slightly modified form of Mulder's method (*Ann. Phys. Chem.*, 1836, 37, 594), and after prolonged extraction with distilled water contained 2.13 per cent. of ash. C=45.01; H=6.32; N=17.15 per cent. The pure compound is completely soluble in water, but concentrated solutions (2 per cent.) have a somewhat cloudy appearance. This soluble form is readily transformed into a sparingly soluble modification under the influence of heat, by evaporation under reduced pressure, and by action of dilute acids. Concentrated hydrochloric acid readily dissolves sericin, concentrated nitric acid only slowly, and concentrated sulphuric acid dissolves it after continuous shaking for 24 hours. Glacial acetic acid dissolves it only slowly and incompletely. Dilute acids (5 per cent. solutions) produce "swelling" at the ordinary temperature, but at 90° dissolve the glue. Sericin dissolves very readily in dilute potassium hydroxide, but not in dilute sodium hydroxide. Most of the resulting solutions contain primary albumoses. A tabular statement of the behaviour of aqueous sericin solutions under different conditions is given. J. J. S.

**Combination of Formaldehyde with Witte's Peptone.** By TORALD SOLLMANN (*Amer. J. Physiol.*, 1902, 7, 220—242).—The addition of formaldehyde to a feebly alkaline solution of Witte's peptone causes the slow development of a precipitate. It is soluble on boiling with dilute acid or alkali, but prolonged contact with the precipitant causes a lessening of its solubility. The solutions give the general reactions of the original proteose and may be reprecipitated by dilute alkali. The precipitate contains both chemically combined and mechanically retained formaldehyde. Only about 40 per cent. of the proteids present participate in the reaction; the primary proteoses are completely precipitated. The formation of the precipitate occurs within narrow limits of reaction, the optimum being 1.1 c.c. normal alkali per gram. In an acid liquid, no combination, and so no precipitation, occurs. Increased alkalinity favours the combination, but as the compound is soluble in alkaline liquids, precipitation is prevented. The formaldehyde and the alkali both enter into the combination in a constant ratio and are liberated in their original quantities by the action of acid. The combination is prevented by the presence of neutral salts.

One gram of Witte's peptone combines with 0.0447 gram of formaldehyde and 6.4 c.c. of decinormal alkali. One gram of the compound contains 0.1109 gram of formaldehyde and 15.9 c.c. of decinormal alkali. The ratio of formaldehyde to alkali is, thus, two equivalents of the former to one of the latter. Since the combined alkali is probably the natural alkalinity of the proteose, it follows that one equivalent of proteose unites with two of formaldehyde. A combination with alkali is also seen with other proteids (compare Benedicenti, *Arch. Physiol.*, 1897, 219, 223). Acacia [*sic.* ? Arabin] does not combine with formaldehyde.

W. D. H.

**Hydrogenases: New Case of Diastatic Hydrogenation.** By M. EMM. POZZI-ESCOT (*Bull. Soc. Chim.*, 1902, [iii], 27, 346—349).—For the purpose of determining whether philothion really possesses the power of hydrogenation, the author has carried out several quantitative experiments on its action on sulphur, whereby he proves that formation of hydrogen sulphide certainly takes place; in the case of selenium and phosphorus, hydrogenation could also be observed, but not, or scarcely so, in the case of arsenic and tellurium. It is also shown that hydrogenases and oxydases mutually decompose one another, a fact which the author holds to plausibly explain the destruction of ceno-oxydase in vinous fermentation. A. F.

**Formation of Oxidation Ferments (Tyrosinase) by Bacteria.** By KARL B. LEHMANN (*Chem. Centr.*, 1902, i, 770; from *Münch. med. Woch.*, 49, 340).—The brown colour of the nutritive medium in which bacteria, such as, for instance, *Bacillus fluorescens non liquefaciens*, has been cultivated, is due to the presence of tyrosinase. When the medium contains sugar, however, it does not become brown. The assumption that by the action of bacteria tyrosine is formed when sugar is not present, and that the tyrosine is then attacked by an oxydase, is supported by the facts that the addition of tyrosine to a culture containing sugar caused it to become brown, and that the colour of a culture free from sugar was intensified by the addition of tyrosine. E. W. W.

**Yeast Trypsin. II.** By FR. KUTSCHER (*Zeit. physiol. Chem.*, 1902, 517—519).—Polemical. Replies to (I) Salkowski (this vol., ii, 165), in which it is stated that the observations made by Salkowski had been previously made by Schützenberger; (II) Hahn and Geret (Abstr., 1901, ii, 677). J. J. S.

**Formation of Zymase in Yeast.** By EDUARD BUCHNER and ALBERT SPITTA (*Ber.*, 1902, 35, 1703—1706).—It has been found by Albert (Abstr., 1899, ii, 783) that when yeast is placed in a 10 per cent. solution of sugar free from nitrogenous nourishment, it yields a more active juice than the unregenerated yeast. If, however, the yeast be taken from the regenerating liquid at the period of most intense fermentation, the juice obtained is less active than that obtained from the original yeast. It has also been found that the amount of zymase contained in yeast decreases when the yeast is preserved in a warm place, but increases when the temperature is kept low. By taking samples of yeast at various times and immediately treating them with alcohol and ether, and then estimating the fermenting power of the yeast as described by Albert, the author finds that when the yeast is exposed to sugar solution for 4—8 hours its fermenting power diminishes, but if it be then pressed and preserved for 2—3.5 hours at a low temperature (0—8°) it increases considerably, in one case by 35 per cent. and in another by 64 per cent. A. H.

## Organic Chemistry.

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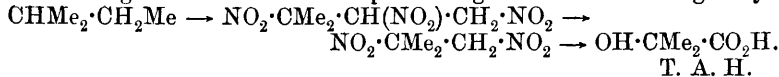
**Synthesis of Various Petroleums ; Theory of the Formation of Natural Petroleums.** By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1902, 134, 1185—1188).—The action of reduced nickel on a mixture of acetylene and hydrogen at a temperature not exceeding 200° yields a highly fluorescent mixture of hydrocarbons which is only slightly attacked by a mixture of nitric and sulphuric acids and has the general physical properties of American petroleum.

If acetylene alone is allowed to act on nickel heated at about 200°, products are formed in the cooler part of the column which condense to a green liquid containing benzene and its homologues and some styrene, together with paraffins and cyclohexanes, and resembling therefore, Caucasian petroleum.

The author suggests that in the interior of the earth alkali and alkali-earth metals are produced, together with their carbides. The action of water on these substances respectively produces hydrogen and acetylene, and these, in contact with finely divided nickel, cobalt, iron, &c., produce hydrocarbons in a manner similar to that described.

C. H. B.

**Action of Nitric Acid on *iso*Pentane.** By PETRUS PONI (*Ann. sci. Univ. Jassy*, 1902, 1, 53—58. Compare *Abstr.*, 1900, i, 617).—The two solid substances previously obtained in this reaction are now shown to be respectively  $\alpha$ -hydroxy*iso*butyric acid and a mixture (melting at 194—197°) of trinitro*iso*pentane and dinitro*iso*butane (compare Francis and Young, *Trans.*, 1898, 73, 928). The author regards the action as proceeding in the following way:



T. A. H.

**New Reactions of Calcium Carbide and Acetylene.** By O. SANDMAN (*Zeit. angew. Chem.*, 1902, 15, 543—545).—A mixture of carbon tetrachloride and acetylene, when passed through a heated glass tube, reacts to form carbon and hydrogen chloride according to the equation  $2\text{C}_2\text{H}_2 + \text{CCl}_4 = 5\text{C} + 4\text{HCl}$ . Analogous results were obtained with carbon disulphide, chloroform, and bromoform, and also when any of these were passed over heated calcium carbide, the bye-products being calcium chloride, bromide or polysulphides, and hydrogen. The action of acetylene on potassium thiocyanate was investigated, the results confirming those of Conroy, Heslop, and Shores (*Abstr.*, 1901, i, 373).

R. H. P.

**Polymerism and Desmotropism of Trimethylethylene Nitrosite.** By JULIUS SCHMIDT (*Ber.*, 1902, 35, 2323—2335. Compare *Abstr.*, 1901, i, 266; this vol., i, 21).— $\beta$ -Methyl- $\beta$ -butylene (*trimethylethylene*)  $\beta$ -nitrosite,  $\text{O}:\text{N} \cdot \text{CHMe} \cdot \text{CMe}_2 \cdot \text{O}:\text{N}:\text{O}$ , obtained by

passing the undried fumes from arsenious oxide and nitric acid into an ethereal solution of  $\beta$ -methyl- $\beta$ -butylene, is a blue oil which decomposes when distilled or even on exposure to diffused light; it has a pungent odour and is insoluble in water, dissolving quite readily, however, in the ordinary organic solvents excepting light petroleum.

The oil gives Liebermann's reaction and at the ordinary temperature partially undergoes polymerisation into *bis-trimethylethylene nitrosite*,  $(C_5H_{10}N_2O_3)_2$ , a solid substance crystallising in white needles and melting at  $75-76^\circ$  to a blue liquid; it is only slightly soluble in ether, glacial acetic acid, or the alcohols, but dissolves more readily in acetone, ethyl acetate, benzene, or ethylene dibromide. The molecular complexity of the two compounds was determined cryoscopically in benzene and ethylene dibromide solutions. The conversion of the original nitrosite into its polymeride is a balanced reaction,  $2C_5H_{10}N_2O_3 \rightleftharpoons (C_5H_{10}N_2O_3)_2$ , and the inverse change occurs on warming the latter compound either alone or in solution, the phenomenon being analogous to that exhibited by nitrogen peroxide  $2NO_2 \rightleftharpoons N_2O_4$ .

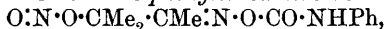
The nitrosite is most readily obtained in a pure state by heating its crystalline polymeride; it neither reacts with phenylcarbimide nor gives a coloration with ferric chloride.

These two nitrosites are at first insoluble in cold solutions of the alkali hydroxides, but they gradually undergo an isomeric change and then dissolve to a yellow solution.

*$\beta$ -Methyl- $\beta$ -butylene  $\beta$ -isositrosite*,  $O:N \cdot O \cdot CMe_2 \cdot CMe:N \cdot OH$ , the product of this intramolecular rearrangement, is precipitated from the alkaline, reddish-yellow solution by dilute sulphuric acid; it is soluble in water or the ordinary organic solvents and crystallises from light petroleum in mossy aggregates of white leaflets melting and decomposing at  $125-126^\circ$ .

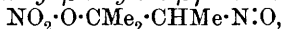
The oxime character of the substance is demonstrated by the production of hydroxylamine by acidic hydrolysis and by its interaction with benzoyl chloride or phenylcarbimide.

The *benzoyl* derivative,  $O:N \cdot O \cdot CMe_2 \cdot CMe:N \cdot OBz$ , obtained by the Schotten-Baumann reaction, crystallises from alcohol in white needles and melts at  $135-136^\circ$ . The *phenylcarbamide* derivative,



produced by mixing its generators in ethereal solution, crystallises from alcohol in white needles decomposing at  $151-152^\circ$ . G. T. M.

**Polymerism of Trimethylethylene Nitrosate.** By JULIUS SCHMIDT (*Ber.*, 1902, 35, 2336—2342. Compare preceding abstract).—On passing the gas evolved from heated lead nitrate into a cold ethereal solution of  $\beta$ -methyl- $\beta$ -butylene, a product is obtained consisting chiefly of oily  *$\beta$ -methyl- $\beta$ -butylene  $\beta$ -nitrosate*,



together with a small amount of solid *bis- $\beta$ -methyl- $\beta$ -butylene nitrosate*. The former of these compounds is a bluish-green oil, decomposing when distilled under reduced pressure and rapidly polymerising into the latter substance. This polymeride, which was first prepared by Guthrie and called "*amylen nitrosate*," crystallises in cubical crystals and melts at  $98-99^\circ$ . The molecular complexity of the compounds



was determined cryoscopically in benzene. A solution of the polymeride begins to exhibit dissociation at 30°, the maximum effect being observed at 60°. At the latter temperature, the solutions of the polymeride in the organic solvents have an intense bluish-green colour, and a molecular weight determination in boiling acetone showed that the substance is present in the unimolecular condition. A cryoscopic determination in naphthalene gave a similar result.

Both the nitrosates give Liebermann's reaction, and the mononitrosate slowly undergoes an isomeric change in the presence of alkali hydroxides and dissolves to a reddish-yellow solution.

G. T. M.

**Flashing Points of Monohydric Fatty Alcohols and their Aqueous Solutions.** By P. N. RAIKOW (*Chem. Zeit.*, 1902, 26, 436—439. Compare Abstr., 1899, i, 47).—The higher the boiling point of an anhydrous monohydric fatty alcohol, the higher its flashing point. On dilution with water, the flashing point rises, the proportional rise at first diminishing to a minimum, then rapidly increasing. In the case of alcohols which are not completely miscible with water, the minimum rise lies between the flashing point of the saturated solution of water in alcohol and that of the saturated solution of alcohol in water.

*tert.*-Butyl alcohol forms an exception, in that on dilution from 50 to 25 per cent. of alcohol the flashing point falls and rises again on further dilution.

G. Y.

**Action of Methyl Alcohol on its Sodium Derivative.** By MARCEL GUERBET (*Bull. Soc. Chim.*, 1902, [iii], 27, 584—585).—Methyl alcohol, when heated with its sodium derivative, does not behave like the other alcohols; at 200°, it remains unchanged, and at 230—240° it decomposes with the formation of gaseous products.

A. F.

**Isomerisation of Unsaturated Alcohols and Saturated Glycols.** By IWAN L. KONDAKOFF (*Chem. Zeit.*, 1902, 26, 469—470. Compare Lieben, this vol., i, 336).—The mechanism of the reactions proposed by Lieben is identical with that previously suggested of the author (*J. pr. Chem.*, 1899, 60, 264).

G. Y.

**Formation of Cuprous Xanthate.** By EINAR BIILMANN (*Ber.*, 1902, 35, 2184—2187).—The interaction of copper sulphate and potassium xanthate gives cuprous xanthate and ethyl dioxithiocarbonate,  $S_2(CS \cdot OEt)_2$ , which can be extracted from the yellow precipitate by ether. The decomposition is thus similar to that of sodium thiosulphate by copper sulphate, which gives sodium cuprous thiosulphate and sodium tetrathionate.

W. A. D.

**Synthesis of Carboxylic Acids.** By JOSEPH HOUBEN and LUDWIG KESSELKAUL (*Ber.*, 1902, 35, 2519—2523).—Details are given of the syntheses of acetic, propionic, benzoic, and phenylacetic acids by passing carbon dioxide into an ethereal solution of the alkyl iodide, which has been treated with metallic magnesium. The yields amounted to about 50 per cent. (except in the case of acetic acid).

R. H. P.

**Compound of Acetic Acid with Nitric Acid.** By AMÉ PICTET and PAUL GENEQUAND (*Ber.*, 1902, 35, 2526—2529).—Nitric acid of sp. gr. 1.4 reacts vigorously with an equal volume of acetic anhydride with the formation of *diacetylorthonitric acid*,  $N(OAc)_2(OH)_3$ , which is a colourless, fuming liquid boiling at  $127.7^\circ$  (corr.) under 730 mm. or at  $45^\circ$  under 17 mm. pressure. It has a sp. gr. 1.197 at  $15^\circ$  and 1.189 at  $23^\circ$ , and  $n_D$  1.38432 at  $23^\circ$ ; it is decomposed by water with development of heat and does not form stable salts.

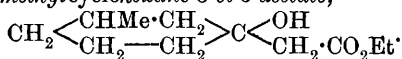
The analogous *dipropionylorthonitric acid* boils at  $140$ — $141^\circ$  under 731 mm. or at  $53$ — $54^\circ$  under 17 mm. pressure and has a sp. gr. 1.114 at  $16^\circ$ .

Attempts to prepare the corresponding formyl, *n*-butyryl, and *iso*-valeryl compounds were not successful.  
R. H. P.

**Reduction of Vinylacrylic Acid.** By JOHANNES THIELE and PAUL JEHL (*Ber.*, 1902, 35, 2320—2321).—When vinylacrylic acid is reduced with sodium amalgam at  $0^\circ$  and the solution is prevented from becoming caustic by the passage of a current of carbon dioxide through it,  $\beta\gamma$ -pentenoic acid and not allylacetic acid (Doebner, this vol., i, 340) is formed; it was identified by its boiling point ( $191$ — $195^\circ$ ) and by its dibromide (m. p.  $65^\circ$ ). Doebner's product initially contained some allylacetic acid, produced by the transformation of the  $\beta\gamma$ -unsaturated acid into  $\alpha\beta$ -unsaturated acid by the sodium hydroxide formed from the amalgam, but this underwent reduction to valeric acid, so that finally a mixture of valeric acid and  $\beta\gamma$ -pentenoic acid was obtained.  
W. A. D.

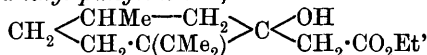
**Application of Sodamide as a Condensing Agent.** By MARTIN FREUND and EDMUND SPEYER (*Ber.*, 1902, 35, 2321—2322).—Ethyl acetoacetate can be prepared by adding finely powdered sodamide to ethyl acetate. Similarly, although acetone is only slowly converted into isophorone by the action of sodium ethoxide, it is immediately acted on by sodamide; the principal product is isophorone, but it is accompanied by mesityl oxide, xylitone, and a viscous substance boiling at  $190$ — $215^\circ$  under 16 mm. pressure.  
W. A. D.

**Condensations with Zinc and Ethyl Iodoacetate.** By LÉON TÉTRY (*Bull. Soc. Chim.*, 1902, [iii], 27, 598—603).—If ethyl iodoacetate is allowed to act on 2-methylcyclohexanone in presence of zinc dust, and the resulting product then treated with water, there is formed *ethyl 1-methylcyclohexane-3-ol-3-acetate*,



It is a colourless, mobile liquid with an agreeable odour, which boils at  $119$ — $120^\circ$  under 9 mm. pressure. When boiled with a solution of zinc chloride in glacial acetic acid, it loses water and forms *ethyl 1-methylcyclo- $\Delta^3$ -hexene-3-acetate*. On saponification with an alcoholic solution of potassium hydroxide, this ester yields the corresponding *1-methylcyclo- $\Delta^3$ -hexene-3-acetic acid*, which forms a colourless oil boiling at  $146^\circ$  under 18 mm. pressure; it has an acid reaction and gives a crystalline salt with copper.

In a similar manner, by the action of ethyl iodoacetate on pulegone, there is obtained *ethyl pulegolacetate*,



a colourless oil boiling at  $142^\circ$  under 9 mm. pressure. The yield is in this case very poor.

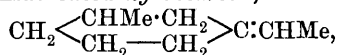
By the condensation of ethyl iodoacetate with citraldehyde, a mixture of substances is apparently obtained, from which, however, ethyl citralideneacetate,  $\text{C}_9\text{H}_{15} \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{Et}$ , can be isolated as a colourless oil with an agreeable odour, which boils at  $129^\circ$  under 9 mm. pressure. From the products of reaction there was also isolated the *lactone*,  $\text{C}_{14}\text{H}_{20}\text{O}_3$ , which forms a colourless oil boiling at  $160^\circ$  under 10 mm. pressure. On saponifying ethyl citralideneacetate with an alcoholic solution of potassium hydroxide, the corresponding acid is obtained; it is a colourless, mobile oil which boils at  $175^\circ$  under 18 mm. pressure, has an acid reaction, and yields a crystalline copper salt. A. F.

**Replacement of Zinc by Magnesium in Certain Synthetical Reactions.** By NICOLAI ZELINSKY and JOHANNES GUTT (*Ber.*, 1902, 35, 2140—2144. Compare *Abstr.*, 1901, i, 661).—Magnesium may with advantage be employed instead of zinc in promoting the condensation of aldehydes or ketones with the esters of the halogen substituted aliphatic acids.

Ethyl 1-methylcyclohexane-3-ol-3-acetate results from the condensation of 1-methylcyclohexane-3-one, and ethyl 1-methylcyclohexane-3-ol-3-propionate is readily obtained from ethyl  $\alpha$ -bromopropionate, 1-methylcyclohexanone, and magnesium; the yield in this case is 30 per cent. of the theoretical, and by employing the corresponding  $\alpha$ -iodo-ester, it may be raised to 45 per cent. When zinc is used as the condensing agent, only a small amount of the required ester is produced.

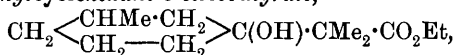
The *intermediate product*,  $2\text{MgBr} \cdot \text{O} \cdot \text{C}_7\text{H}_{12} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}, \text{Et}_2\text{O}$ , is a crystalline substance soluble in benzene, but not in light petroleum.

By digesting the preceding substituted propionate with crystallised oxalic acid, an unsaturated *ester*,  $\text{CH}_2 \begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{C} : \text{CMe} \cdot \text{CO}_2\text{Et}$ , is obtained, which boils at  $103\text{--}104^\circ$  under 11 mm. pressure, and has a sp. gr. 0.9487 and  $n_D$  1.4606 at  $16^\circ$ , and  $[\alpha]_D + 48.41^\circ$ . Prolonged treatment with oxalic acid leads to further change, resulting in the production of the unsaturated *hydrocarbon*,



a compound boiling at  $150\text{--}151^\circ$  under 738 mm. pressure; it has a sp. gr. 0.8154, and  $n_D$  1.4538 at  $19^\circ$ , and  $[\alpha]_D + 56.63^\circ$ .

*Ethyl 1-methylcyclohexane-3-olisobutyrate*,



obtained by the interaction of 1-methylcyclohexane-3-one and ethyl  $\alpha$ -bromoisobutyrate in the presence of magnesium, boils at  $131\text{--}132^\circ$  under 13 mm. pressure; it has a sp. gr. 1.000 and  $n_D$  1.4626 at  $18^\circ$ , and  $[\alpha]_D + 0.24^\circ$ ; this substance could not be isolated in a pure state by the use of zinc.

The unsaturated ester,  $\text{CH}_2 \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 \text{---CH} \end{smallmatrix} \text{C} \cdot \text{CMo}_2 \cdot \text{CO}_2\text{Et}$ , results from the action of crystallised oxalic acid on the preceding compound; it boils at  $110\text{--}112^\circ$  under 11 mm. pressure, has a sp. gr. 0.9460 and  $n_D$  1.4619 at  $18^\circ$ , and  $[\alpha]_D +45.59^\circ$ .

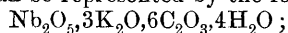
*Ethyl cycloheptane-1-olacetate*,  $\begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , produced by condensing suberone with ethyl  $\alpha$ -bromoacetate with magnesium suspended in absolute ether, boils at  $133\text{--}134^\circ$  under 11 mm. pressure; it has a sp. gr. 1.0392 and  $n_D$  1.4686 at  $17^\circ$  (compare also this vol., i, 370 and 341). G. T. M.

**Alkali Cobaltioxalates.** By COPAUX (*Compt. rend.*, 1902, 134, 1214—1216).—By dissolving cobaltous oxalate in a solution of the alkali oxalate, and adding the calculated quantity of lead peroxide and some acetic acid, the author has prepared the following cobaltioxalates,  $(\text{NH}_4)_6\text{Co}_2(\text{C}_2\text{O}_4)_6 \cdot 6\text{H}_2\text{O}$  (monoclinic),  $\text{K}_6\text{Co}_2(\text{C}_2\text{O}_4)_6 \cdot 7\text{H}_2\text{O}$  (triclinic),  $\text{Rb}_6\text{Co}_2(\text{C}_2\text{O}_4)_6 \cdot 8\text{H}_2\text{O}$  (rhombic),  $\text{Na}_6\text{Co}_2(\text{C}_2\text{O}_4)_6 \cdot 10\text{H}_2\text{O}$  (monoclinic),  $\text{Li}_6\text{Co}_2(\text{C}_2\text{O}_4)_6 \cdot 12\text{H}_2\text{O}$  (triclinic),  $\text{K}_5\text{Na}_{19}\text{Co}_8(\text{C}_2\text{O}_4)_{24} \cdot 32\text{H}_2\text{O}$  (pseudocubic),  $\text{Na}_3\text{Rb}_3\text{Co}_2(\text{C}_2\text{O}_4)_6 \cdot 5\text{H}_2\text{O}$  (monoclinic),  $\text{Na}_3(\text{NH}_4)_3\text{Co}_2(\text{C}_2\text{O}_4)_6 \cdot 7\text{H}_2\text{O}$  (monoclinic).

These salts are green, opaque, and dichroic; they dissolve in water, but dilute solutions decompose gradually at the ordinary temperature, and immediately on boiling, with precipitation of cobaltous oxalate. The solutions give no precipitate with calcium chloride, but are immediately, although partially, decomposed by alkali hydroxides. The ammonium, potassium, and rubidium salts are not isomorphous as in the iron, chromium, aluminium series. C. H. B.

**Niobioxalic Acid.** By FRANZ RUSS (*Zeit. anorg. Chem.*, 1902, 31, 42—91).—The author gives an historical account of the complex metallo-oxalates which have been prepared, and as a criterion of the complexity he takes the stability of the ammonium compounds in water.

The niobic acid used in the investigation was extracted from Norwegian columbite by a modified form of Marignac's method. By fusing niobic acid with potassium carbonate and dissolving the residue in water, then adding oxalic acid and evaporating, a solid substance separates out which can be represented by the formula



it can be recrystallised from water. Attempts to prepare other potassium niobioxalates were fruitless. The corresponding sodium salt,  $\text{Nb}_2\text{O}_5 \cdot 3\text{Na}_2\text{O} \cdot 6\text{C}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ , was prepared in a similar manner. It forms supersaturated solutions much more easily than the potassium salt. The ammonium salt,  $\text{Nb}_2\text{O}_5 \cdot 3(\text{NH}_4)_2\text{O} \cdot 6\text{C}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , was obtained by fusing niobic oxide with potassium carbonate and decomposing the niobate with hydrochloric acid; the hydrated niobic acid was then dissolved in a solution of ammonium binobate. From the solution, large crystals of the ammonium salt separate on cooling, and it can be completely precipitated by the addition of acetone. The

rubidium salt,  $\text{Nb}_2\text{O}_5, 3\text{Rb}_2\text{O}, 6\text{C}_2\text{O}_3, 4\text{H}_2\text{O}$ , which is very easily soluble in water, was prepared in the same way as the potassium salt.

From a solution of niobic acid containing excess of oxalic acid there crystallises a niobioxalic acid of the formula  $\text{Nb}(\text{C}_2\text{O}_4\text{H})_5$ , which, however, is decomposed by water. By treatment with alcohol, a residue of the unstable compound,  $\text{Nb}_2\text{O}_5, \text{C}_2\text{O}_3, 4\text{H}_2\text{O}$ , has also been obtained.

A solution of potassium niobioxalate gives precipitates with solutions of barium, strontium, and calcium salts; the precipitated barium salt has the formula  $\text{Nb}_2\text{O}_5, 5\text{BaO}, 10\text{C}_2\text{O}_3, 20\text{H}_2\text{O}$ . The following ions also give precipitates:  $\text{Fe}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Cr}^{+++}$ ,  $\text{Cu}^{++}$ ,  $\text{UO}_2^{+}$ ,  $\text{Ag}^{+}$ ,  $\text{Hg}^{+}$ , and  $\text{Pb}^{++}$ , whilst  $\text{Mn}^{++}$ ,  $\text{Zn}^{++}$ , and  $\text{Hg}^{++}$  do not. When heated in a current of chlorine, carbon tetrachloride, or hydrogen chloride, potassium niobioxalate leaves a residue of potassium chloride and niobic oxide. When heated in a current of carbon disulphide, a residue is left which contains carbon, a potassium polysulphide, and a niobium compound containing sulphur, but of composition varying with the conditions of the experiment.

From the results of conductivity measurements with polished platinum electrodes (platinised electrodes cause a catalytic decomposition), it is deduced that the salts are hydrolysed in aqueous solution.

No positive result was obtained in an attempt to effect the separation of niobium and tantalum by means of the complex oxalates.

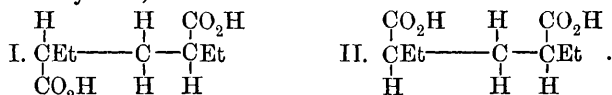
J. McC.

**Complex Salts of Osmium: Potassium Osmyloxalate.** By MAURICE VÉZES and L. WINTREBERT (*Bull. Soc. Chim.*, 1902, [iii], 27, 569—578).—If osmium peroxide, dissolved in an aqueous solution of pure potassium hydroxide, is treated with excess of oxalic acid, and the solution thus obtained heated to boiling in a flask fitted with an upright condenser until vapours of peroxide cease to be disengaged (several hours), a crystalline deposit of potassium osmyloxalate separates from the liquid on cooling. The yield is practically quantitative. The same compound is also formed by adding excess of oxalic acid to a hot concentrated solution of potassium oxalate, or by digesting osmium peroxide with a concentrated solution of potassium dioxalate in the cold. This salt, which has the formula  $\text{K}_2\text{OsO}_2(\text{C}_2\text{O}_4)_2, 2\text{H}_2\text{O}$ , forms triclinic crystals showing dichroism (yellowish-green and brownish-yellow); in the dry state, the crystals are comparatively stable, but on heating at  $80^\circ$  lose their water of crystallisation. On heating more strongly, decomposition occurs, carbon dioxide is evolved, and a mixture of osmium protoxide and potassium carbonate is left. Potassium osmyloxalate is very sparingly soluble in cold water, but the solubility increases with rise of temperature; it is almost insoluble in a solution of potassium chloride. In aqueous solution in the cold, more quickly on heating, potassium osmyloxalate slowly decomposes with formation of osmic acid; this decomposition is prevented by the presence of a small quantity of potassium oxalate, oxalic acid, or hydrogen potassium oxalate. When treated with ammonia, a yellow, crystalline precipitate

of osmyldiammonium oxalate (Abstr., 1882, 144) is produced, and on being treated with hydrochloric acid chlorine is evolved and potassium chloro-osmate formed.

A. F.

*s*-*aa*-Diethylglutaric Acid and its Preparation from the Corresponding  $\beta$ -Hydroxy-acid. By SERGIUS N. REFORMATSKY (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 357—370).—Two symmetrical *aa*-diethylglutaric acids were prepared by Auwers (Abstr., 1896, i, 639), one melting at 118—119° and the other at 76—78°, but the individuality of the latter was not established. The first of these acids has been obtained in large quantity by the author by preparing the corresponding  $\beta$ -hydroxy-acid and acting on this with hydriodic acid. It is found that the acid obtained in this way melts at 119·5—120°, and when treated with nitric acid is partially converted into a stereoisomeric modification melting at 93·5—94·5°. The latter is shown to be the fumaric form of *s*-*aa*-diethylglutaric acid having the structure I, whilst the other, melting at 119·5—120°, which readily forms an anhydride, is the maleic modification of the constitution II:



The acid melting at 76—78°, described by Auwers (*loc. cit.*), consists of a mixture of the two above stereoisomerides.

*s*-Ethyl  $\beta$ -hydroxy-*aa*-diethylglutarate,  $\text{OH}\cdot\text{CH}(\text{CHEt}\cdot\text{CO}_2\text{Et})_2$ , obtained by the action of zinc on a mixture of ethyl formate and ethyl  $\alpha$ -bromobutyrate, is a colourless liquid which boils at 283—284° and readily dissolves in alcohol or ether; it has the normal molecular weight in boiling ether, a sp. gr. of 1·01682 at 20°/4°, 1·01018 at 22·4°/4°, 1·00899 at 24·3°/4°, and 1·00675 at 25·9°/4°;  $n_D$  at 20°, 1·4405. The corresponding acid was obtained as a pale yellow syrup, soluble in water, alcohol, or ether. The *barium* salt, with  $2\text{H}_2\text{O}$ , was prepared and analysed.

The maleic form of *aa*-diethylglutaric acid crystallises from water in large, shining, monoclinic prisms [ $a:b=1\cdot261:1$ ;  $\beta=76^\circ7'$ ].

The fumaric modification, melting at 93·5—94·5°, separates from aqueous solution in monoclinic crystals, which are more readily soluble in water than those of the stereoisomeride; [ $a:b:c=0\cdot8848:1\cdot2\cdot2743$ ;  $\beta=75^\circ20'$ ]. The *potassium* salt was prepared and analysed.

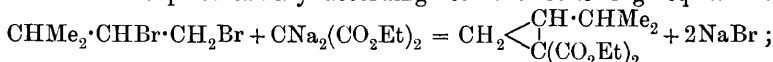
The relations between the three *s*-*aa*-diethylglutaric acids, melting at 119·5—120°, 93·5—94·5°, and 76—78° respectively, are thus similar to those existing in the case of the corresponding dimethyl acids melting at 140—141°, 127—128°, and 102—104°; with the latter acids, however, the maleic modification has a lower melting point than the fumaric form.

T. H. P.

Action of Ethyl Sodiomalonate on the Dibromides  $\text{C}_n\text{H}_{2n}\text{Br}_2$ . III. By WLADIMIR IPATIEFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 351—356. Compare Abstr., 1899, i, 481 and 673).—The action of ethyl sodiomalonate on  $\alpha\gamma$ -dibromo- $\beta$ -dimethylpropane gives rise to a

crystalline *ester* melting at 105—105.5°; the corresponding *acid*,  $C_7H_8O_4$ , decolorises potassium permanganate and gives a *bromo-derivative* melting at 127—128°. The structure of the acid has not yet been ascertained.

The interaction of ethyl sodiomalonate and  $\alpha\beta$ -dibromo- $\gamma$ -methylbutane takes place mainly according to the following equation:



the *ester*,  $C_{12}H_{20}O_4$ , which is thus obtained, together with traces of ethyl ethanetetracarboxylate, boils at 122—132° under 18 mm. pressure, and the corresponding *isopropyltrimethylenedicarboxylic acid* separates from chloroform in crystals melting at 76—78° and is soluble in water, benzene, or ether; it does not decolorise permanganate solution or combine directly with bromine, and when heated at its melting point it loses carbon dioxide, giving *isopropyltrimethylenedicarboxylic acid*; its *potassium*, *calcium*, and *silver* salts were prepared.

[With S. BORDELIUS.]—The action of ethyl sodiomalonate on  $\psi$ -butylene dibromide yields bromobutylene,  $CHMe \cdot CBrMe$ , and a small quantity of ethyl ethanetetracarboxylate. With *isobutylene* dibromide, ethyl sodiomalonate gives *isobutylene*, bromo*isobutylene*,  $CMe_2 \cdot CHBr$ , and ethyl ethanetetracarboxylate.

[With W. MICHAELADZE.]—The action of ethyl sodiomalonate on  $\alpha\gamma$ -dibromobutane gives traces of a bromo-compound together with *diethyl methyltetramethylenedicarboxylate*, which is formed according to the equation:  $CHMeBr \cdot CH_2 \cdot CH_2Br + CNa_2(CO_2Et)_2 = 2NaBr + CHMe \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} C(CO_2Et)_2$ ; this ester boils at 155—165° under 15 mm.

pressure, and the corresponding *acid*,  $C_7H_{10}O_4$ , separates from chloroform in crystals, which melt at 157—158° and are soluble in water, alcohol, ether, or benzene; the *potassium*, *ammonium*, *calcium*, and *silver* salts were prepared.

The author draws the following conclusions concerning the course followed by the reaction between ethyl sodiomalonate and dibromides: (1) Dibromides in which the bromine atoms are attached to neighbouring carbon atoms only yield closed-chain trimethylene acids when the carbon atoms to which the bromine atoms are joined are either both primary or one primary and the other secondary. (2) Dibromides in which the bromine atoms are combined either with two secondary, or with one primary and one tertiary, carbon atoms give no acid, but mostly an unsaturated bromide; when the carbon atoms in question are secondary and tertiary respectively, there are formed, besides an unsaturated bromide, a hydrocarbon of the ethylene series and ethyl ethanetetracarboxylate. (3) Dibromides in which the bromine atoms are joined to two carbon atoms separated by another carbon atom yield closed-chain tetramethylene acids in cases where these carbon atoms are either both primary or one primary and the other secondary; if one of the carbon atoms is tertiary, the reaction gives an unsaturated substituted *gem*.-allylmalonic acid. T. H. P.

**Camphoric Acid. XI. Confirmation of Bredt's Formula; some Derivatives of Inactive Camphoric Acid.** By WILLIAM A. NOYES and AUSTIN M. PATTERSON (*Amer. Chem. J.*, 1902, 27, 425—433).—Dihydro- $\alpha$ -campholytic acid (Abstr., 1901, i, 664) has been carried through the same series of transformations as dihydro- $\beta$ -campholytic acid (Abstr., 1899, i, 284), namely, conversion into bromo-derivative, saponification into hydroxy-compound, elimination of carbon dioxide, and finally, formation of oxime. The *oxime* is that of 2:2:3-trimethylcyclopentanone, and it crystallises in plates which melt at 104°. It is shown that this result, in conjunction with that previously obtained, can only be explained by Bredt's formula. Some reactions of  $\alpha$ -campholytic acid are pointed out which cannot readily be explained by current stereochemical theories.

From a specimen of artificially prepared inactive camphor (m. p. 176°)  $\beta$ -camphoramidic acid,  $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}\cdot\text{NH}_2$ , has been prepared by passing ammonia through an alcoholic solution and treating the resulting product with sodium hydroxide; it crystallises in needles which melt at 178°.

i-Aminodihydrocampholytic acid,  $\text{NH}_2\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}_2\text{H}$ , prepared by the method adopted for the active isomeride (Abstr., 1895, i, 187), crystallises in leaflets which closely resemble the active modification. The *anhydride* melts at 188°.

When treated with 0.5 mol. of sulphuric acid and 1 mol. of sodium nitrite, the amino-acid decomposes and gives i-dihydrocampholytic acid which melts at 173° and i- $\alpha$ -campholytic acid which was obtained as a liquid. J. McC.

**Preparation of Malic Acid from Stems of Rhubarb.** By NICOLA CASTORO (*Landw. Versuchs-Stat.*, 1902, 56, 423—424).—The acid was separated as the strontium salt. This salt did not crystallise in nodules containing  $1\frac{1}{2}$  mols.  $\text{H}_2\text{O}$  as usually described, but in needles, or sometimes in plates, and contained  $4\text{H}_2\text{O}$ .

N. H. J. M.

**Substitution of Hydrogen for Chlorine in Trichloromethylparaconic Acid.** By HENRY C. MYERS (*J. Amer. Chem. Soc.*, 1902, 24, 525—528).—The author has shown (Trans., 1897, 71, 614) that when trichloromethylparaconic acid is reduced with zinc dust or sodium amalgam, dichloromethylparaconic acid is obtained. If, however, the reduction with sodium amalgam is continued for 7—10 days, the products consist of dichloromethylparaconic acid, chlorodiparaconic acid, and an *acid* which resembles benzoic acid in appearance and melts at 126—127°. When chlorodiparaconic acid is heated above its melting point, it suffers decomposition with elimination of a molecular proportion of hydrogen chloride. E. G.

**The Degradation of Rhamnonic and isoSaccharic Acids.** By OTTO RUFF (*Ber.*, 1902, 35, 2360—2370).—[With HUGO KOHN].—Calcium rhamnonate,  $\text{Ca}(\text{C}_6\text{H}_{11}\text{O}_6)_2$ , obtained as a white, stable salt by oxidising rhamnose with an aqueous suspension of bromine, and treating the product successively with lead carbonate, silver oxide,



and calcium carbonate, is precipitated from the concentrated final mother liquor by adding alcohol. This salt, when treated with ferric acetate and hydrogen peroxide, is oxidised to methyltetrose, which is isolated in the form of its *phenylbenzylhydrazone* by adding an alcoholic solution of phenylbenzylhydrazine to the crude syrupy sugar dissolved in the same solvent. This hydrazone crystallises from benzene or alcohol in needles melting at 96—97°; it has  $[\alpha] - 6.5^\circ$  for white light.

Methyltetrose is produced by decomposing the preceding compound with 40 per cent. formaldehyde solution and obtained in the form of a syrup exhibiting multirotation. The freshly prepared solution has  $[\alpha]_D - 30.5^\circ$ , this value diminishes and after 4 hours remains constant at  $-16.35^\circ$ . When treated with sodium diazobenzenesulphonate, the sugar develops a violet coloration and is therefore an aldose; it yields an *ethyl-mercaptal*,  $C_9H_{20}O_3S_2$ , by condensation with ethyl mercaptan in the presence of concentrated hydrochloric acid; this derivative crystallises in white, tasteless, and odourless needles melting at 108—109°.

*Methyltetronic acid*, produced by oxidising methyltetrose with bromine, separates from aqueous solution in the form of its *lactone*, a substance crystallising in needles and having  $[\alpha]_D - 47.5^\circ$ . All the metallic methyltetronates excepting the copper salt are amorphous, and the latter, although crystallising in needles, is unstable when heated on the water-bath. The *brucine* salt, however, crystallises well from absolute alcohol in needles melting at 145—150°; it is readily soluble in water but dissolves more sparingly in the ordinary organic solvents. Other alkaloids also yield well crystallised methyltetronates.

The *phenylhydrazone* crystallises from ethyl acetate in silky, snow-white leaflets and melts at 169° (corr.).

[With ADOLF MEUSSER and ARTHUR FRANZ.]—When treated in aqueous solution with hydrogen peroxide and ferric acetate, lead *iso-saccharate* gives rise to a new ketose (*pentanetriolone*), which is obtained in the form of a syrup after evaporating the filtered mother liquors under diminished pressure. The ketose has  $[\alpha]_D - 36^\circ$  and does not develop a coloration with sodium diazobenzenesulphonate. The *osazone* crystallises from benzene in needles containing benzene of crystallisation; the latter is removed at 80°, and the compound melts at 125°; it is soluble in the ordinary organic solvents excepting petroleum and is optically inactive. The *phenylbenzylhydrazone*,  $C_{18}H_{22}O_3N_2$ , of the pentanetriolone, formed by heating its generators dissolved in dilute alcohol, crystallises from benzene or water in pale yellow needles, melting at 124—126° and decomposing at 200°; it is readily soluble in hot water or the ordinary organic solvents excepting light petroleum and is optically inactive. The ketose yields an uncrystallisable oxime, and on reduction with sodium amalgam gives rise to a mixture of the two pentaerythritols.

G. T. M.

**Synthesis of Aldehydes of the Acetic Series by means of Nitromethane.** By LOUIS BOUVEAULT and ANDRÉ WAHL (*Compt. rend.*, 1902, 134, 1226—1228).—When the compounds  $R \cdot CH(OH) \cdot CH_2 \cdot NO_2$ , obtained by Henry by the condensation of aldehydes of the acetic series

with nitromethane, are dehydrated by boiling their acetic acid solutions with zinc chloride, they yield nitrohydrocarbons of the type  $R \cdot CH : CH \cdot NO_2$ . When the latter are reduced with aluminium amalgam or with zinc and acetic acid, they yield oximes,  $R \cdot CH_2 \cdot CH : N \cdot OH$ .

The product of the condensation of valeraldehyde and nitromethane described by Henry yields *nitroisohexylene*,  $CHMe_2 \cdot CH_2 \cdot CH : CH \cdot NO_2$ , when dehydrated; it is a pale yellow liquid which boils at 80—81° under 10 mm. pressure, volatilises in steam, has a very pungent odour, and a sp. gr. 0.995 at 0°/0°. When reduced, it yields *isohexaldoxime*, a colourless liquid with a disagreeable odour which boils at 90—91° under 20 mm. pressure, has a sp. gr. 0.910 at 0°/0°, and when hydrolysed, yields *isohexaldehyde*. Heptaldehyde and nitromethane yield a pale yellow liquid boiling at 138—140° under 10 mm. pressure with slight decomposition, and its dehydration product is *nitro-octylene*,  $CH_3 \cdot [CH_2]_5 \cdot CH : CH \cdot NO_2$ , a pale yellow liquid which has a very disagreeable odour, boils at 113—115° under 8 mm. pressure, and has sp. gr. 0.970 at 0°/0°. When reduced, it yields *octaldoxime*,  $CH_3 \cdot [CH_2]_6 \cdot CH : NOH$ , which melts at 56°, boils at 120—125° under 10 mm. pressure, and yields octaldehyde when hydrolysed.

C. H. B.

**Study of Methyl Nonyl Ketone, Methyl Heptyl Ketone, and their corresponding Secondary Alcohols.** By C. MANNICH (*Ber.*, 1902, 35, 2144—2146).—Methyl heptyl ketone and methyl nonyl ketone, both contained in oil of rue, are readily reduced, yielding the corresponding secondary alcohols.

*Methylheptylcarbinol* boils at 87.5° under 10 mm. pressure and at 193—194° under the ordinary pressure. *Methylnonylcarbinol* boils at 120° under 14 mm. pressure; its *acetyl* derivative boils at 147—149° under 42 mm., and the *benzoyl* derivative at 197.5—200° under 15 mm. pressure. The *phenylcarbamate* and the *oxalate* of the latter carbinol melt at 36.5—37° and 34.5° respectively.

When dehydrating agents act on these alcohols,  $\Delta^{\beta}$ -olefine derivatives are formed, the removal of water taking place between the second and third carbon atoms of the chain.

$\Delta^{\beta}$ -*Undecylene*,  $C_{11}H_{22}$ , boils at 192—193° and yields a colourless, oily *dibromide*,  $C_{11}H_{22}Br_2$ , boiling at 145—146° under 9 mm. pressure; the latter substance on treatment with potassium hydroxide loses hydrogen bromide and gives rise to  $\beta\gamma$ -*undecinenene*,  $C_{11}H_{20}$ , a colourless liquid boiling at 81.5° under 10 mm. and at 199—201° under the ordinary pressure; this hydrocarbon has an unpleasant odour.

*Methylnonylcarbinol*, when subjected to the action of dehydrating agents, gives rise to the *ether*,  $(C_{11}H_{23})_2O$ , a light yellow liquid boiling at 198—200° under 10 mm. pressure.

*Undecylene dibromide*, on treatment with silver acetate, yields *undecane- $\beta\gamma$ -diol*, a compound separating in crystals having a greasy lustre and melting at 51—53°.

$\Delta^{\beta}$ -*Nonylene* boils at 147—148° under the ordinary pressure.

When reduced, the oximes of methyl nonyl ketone and methyl heptyl ketone yield the corresponding amines,  $\beta$ -*undecylamine* and  $\beta$ -*nonyl-*

*amine*, boiling respectively at 113—114° under 26 mm., and at 69—70° under 11 mm. pressure.

The *ketone*,  $C_9H_{19} \cdot CMe \cdot CH \cdot CO \cdot C_9H_{19}$ , is produced by saturating methyl nonyl ketone with hydrogen chloride and distilling the oily additive product,  $C_{22}H_{43}OCl$ , under diminished pressure; it boils at 214—216° under 10 mm. pressure, and although its phenylhydrazone and semicarbazone are oily, yet the *picrate* of its aminoguanidine compound is crystalline and melts at 125—126°. The unsaturated ketone is not affected by 10 per cent. sulphuric acid, but a stronger solution (60 per cent.) reconverts it into methyl nonyl ketone. G. T. M.

**Behaviour of Diketones towards Organo-magnesium Compounds.** By NICOLAI ZELINSKY (*Ber.*, 1902, 35, 2138—2140).—Di-acetyl, when mixed with a cold suspension of magnesium methiodide in absolute ether, is readily converted into pinacone, the product being characterised by its boiling point (171—173°), and the crystalline hydrate melting at 46°.

Acetylacetone and the organo-magnesium compound interact energetically, but the yield of product is only small and consists of a glycol corresponding in composition with the formula  $C_7H_{16}O_2$ , and boiling at 100—102° under 16 mm. pressure.

Acetonylacetone, when similarly treated, gives a quantitative yield of  $\beta\epsilon$ -dimethylhexane- $\beta\epsilon$ -diol,  $OH \cdot CMe_2 \cdot CH_2 \cdot CH_2 \cdot CMe_2 \cdot OH$ , a glycol soluble in the ordinary organic solvents and crystallising in long prisms melting at 92—93°; these crystals, when separating from benzene or toluene, exhibit a greenish-violet fluorescence while remaining in contact with the mother liquor.

The dibromide,  $C_8H_{16}Br_2$ , obtained by the action of a glacial acetic acid solution of hydrogen bromide on the glycol, crystallises from light petroleum in prisms melting at 71—72°. G. T. M.

**Behaviour of Araban with Fehling's Solution.** By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1902, 35, 240—245. Compare Salkowski, this vol., i, 206).—The author finds that his previous statement, that araban in alkaline solution is not precipitated by Fehling's solution, is inaccurate. A solution in dilute sodium hydroxide, containing 8 per cent. of this substance prepared from gum arabic, is precipitated on addition of one-fifth of its volume of Fehling's solution, but if the amount of the latter be increased to one-third, only a slight precipitate is formed, whilst with equal volumes of the two liquids a clear mixture is produced, the precipitate being soluble in excess of the reagent. The corresponding xylan precipitate does not appear to be soluble in excess. The author's previous experiments were carried out with araban obtained from beet-root, which was not precipitated by addition of about one-third of its volume of Fehling's solution, whence he concludes either that this araban is not identical with that contained in gum arabic, or that it had undergone some change during preparation. The latter supposition is, he considers, the more probable, although it is not in accordance with the fact that araban, prepared by the same process from gum arabic, undergoes no change.

T. A. H.

**Crystallised Stachyose.** By ERNST SCHULZE (*Landw. Versuchs-Stat.*, 1902, 56, 419—423. Compare *ibid.*, 40, 218).—By slightly modifying the process previously employed, stachyose was obtained in large, colourless, lustrous plates, probably triclinic. The crystals only contain traces of mineral matters. The composition of the crystals corresponds with the formula  $C_{18}H_{32}O_{16}, 3H_2O$ .

Stachyose containing water of crystallisation gives  $[\alpha]_D + 133.5^\circ$ ; nearly the same number ( $+135^\circ$ ) is obtained with a 10 per cent. aqueous solution of uncrystallised air-dried stachyose at  $16^\circ$ .

N. H. J. M.

**Behaviour of Silver Haloids with Organic Amino-bases.** By BERTHOLD WUTH (*Ber.*, 1902, 35, 2415—2420).—The solubility of silver chloride and bromide in aqueous methylamine or ethylamine has been determined (compare Bodländer and Fittig, this vol., ii, 248). In both cases, the solubility increases with increase of the concentration of the base, but when the results are expressed on a system of ordinates, the solubility curve in methylamine is concave to the abscissa, whereas that in ethylamine is convex to that axis. It appears most probable that in methylamine the complexes  $3AgCl, NH_2Me$  and  $3AgBr, NH_2Me$  are present.

The double salt,  $AgBr(C_5NH_5, HBr)_2$ , is prepared by adding the double salt of silver chloride and pyridine hydrochloride to a boiling concentrated solution of potassium bromide; it forms a white, crystalline powder which is decomposed by water. The corresponding double *iodide* crystallises in needles. Silver and piperidine form a double *chloride*,  $AgCl(C_5NH_{11}, HCl)_3$ , and a double *bromide* which crystallises from chloroform in white leaflets, and a double *iodide* which crystallises in needles (compare Renz, this vol., i, 563). K. J. P. O.

**Transformation of Glyoxylic Acid into Glycine by the Action of Ammonia.** By EMIL ERLÉNMEYER and JULIUS KUNLIN (*Ber.*, 1902, 35, 2438—2440).—Just as phenylpyruvic acid reacts with ammonia yielding phenylacetylphenylalanine ( $\alpha$ -phenylacetyl-amino- $\beta$ -phenylpropionic acid) (Abstr., 1899, i, 761), and pyruvic acid and ammonia give  $\alpha$ -acetylaminopropionic acid with elimination of water and carbon dioxide (de Jong, Abstr., 1901, i, 130), so do glyoxylic acid and ammonia produce formylaminoacetic acid when heated together at  $100^\circ$ . Formylaminoacetic acid was not isolated from the oily product of the reaction, but on hydrolysing with hydrochloric acid, formic acid and glycine were isolated; the latter was obtained as the copper salt, and by interaction with benzaldehyde and acetic anhydride was converted into the azlactone (see next page). K. J. P. O.

**Amino-acids of the  $C_nH_{2n+1}O_2N$  Series.** By FRIEDRICH KUTSCHER (*Sitzungsber. K. Akad. Wiss. Berlin.*, 1902, 588—592).—To prepare the silver salts of the amino-acids of this series, a solution of silver nitrate is added in very slight excess to an aqueous solution of the acid, then a cold saturated solution of barium hydroxide is added with continual shaking. Silver oxide is at first precipitated, then redissolves, and the silver salt separates in a crystalline form.

In this way, the silver salts of glycine, aminovaleric acid, and leucine have been obtained; it has not been possible to prepare the salts of  $\alpha$ -alanine or sarcosine. The method may possibly be useful for separating the decomposition products of albumin. J. McC.

**Amino-acids prepared from Plants.** By ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1902, **35**, 299—314).—Methods for the preparation of amino-acids from plants are described, and several of the more common substances of this class have been re-examined, and especially their specific rotations and solubilities re-determined, with results generally in accordance with those of previous observers. The authors show that the aminovaleric acid occurring in *Lupinus* species is identical with that obtained by E. Fischer (*Abstr.*, 1901, i, 780) as a hydrolytic product of casein, and that the seedlings of *Vicia sativa* contain, in addition to leucine, an isomeride of the latter differing from it by having a higher specific rotation. T. A. H.

**Azlactones and the Conversion of Pyrrolic Acid into Methylpyruvic Acid.** By EMIL ERLÉNMEYER, jun. (*Ber.*, 1902, **35**, 2483—2486. Compare *Abstr.*, 1900, i, 549).—The compounds formed by the condensation of aldehydes with hippuric acid have probably the

formula  $R \cdot CH : C \begin{matrix} \nearrow N=CPh \\ \searrow CO-O \end{matrix}$ , and the author therefore terms them

*azlactones*, from analogy with the unsaturated  $\beta$ -lactones formed from  $\gamma$ -ketonic acids. This constitution is confirmed by the behaviour of the condensation product of pyruvic acid with hippuric acid, which was first described by Hoffmann (*Ber.*, 1886, **19**, 2554). This substance dissolves in aqueous sodium carbonate, a salt of the formula  $CO_2Na \cdot CMe : C(CO_2Na) \cdot NH \cdot CPh$  being formed; when the solution is acidified in the cold, no precipitate is formed, the corresponding dibasic acid being soluble, but when the liquid is heated, the  $\beta$ -azlactone is at once re-formed and precipitated. When the azlactonecarboxylic acid is heated for some time with hydrochloric acid, it is completely hydrolysed, yielding benzoic acid and methylpyruvic acid, formed from the benzamide and methylxaloacetic acid, which are the primary products. This reaction affords a method for passing from an  $\alpha$ -ketonic acid to the next higher homologous acid. Phenylpyruvic acid, however, and certain of its derivatives do not appear to undergo this reaction, which is being applied to other acids of the same type. A. H.

**Dithiocarbamic Esters derived from Primary Amines.** By MARCEL DELÉPINE (*Compt. rend.*, 1902, **134**, 1221—1223).—The preparation of esters of the dithiourethanes of the general formula  $RNH \cdot CS \cdot SR'$  is simplified by allowing 1 mol. proportion of a haloid ester to act on the thiocarbamic derivatives of the primary amines  $NHR \cdot CS \cdot S \cdot NH_3R + XR' = NHR \cdot CS \cdot SR' + X \cdot NH_3R$ . In the case of amines such as those of the benzene series, which are only slightly basic, it is better to adopt the Losanitsch's method and allow the amine to act on a mixture of carbon disulphide and ammonia, yielding a compound,  $RNH \cdot CS \cdot SNH_4$ , which is readily acted on by the haloid ester. This method is also applicable to secondary amines, yielding compounds

such as  $\text{NMePh}\cdot\text{CS}_2\cdot\text{NH}_4$ ,  $\text{NEtPh}\cdot\text{CS}_2\cdot\text{NH}_4$ , from which the dithiourethanes are readily obtained.

The author has prepared a number of mono-substituted dithiourethanes, and confirms Hoffmann's statement that when heated they readily split up into a thiocarbimide and mercaptan. With a further mol. proportion of haloid ester, they yield compounds such as  $\text{NMe}\cdot\text{C}(\text{SMe})\cdot\text{SEt}$  and  $\text{NMe}\cdot\text{C}(\text{SMe})\cdot\text{S}\cdot\text{CH}_2\text{Ph}$ . With ammonia and substituted ammonias, the reaction  $\text{R}\cdot\text{NH}\cdot\text{CS}\cdot\text{SR}' + \text{NHR}''\text{R}''' = \text{R}\cdot\text{NH}\cdot\text{CS}\cdot\text{NR}''\text{R}''' + \text{HS}\cdot\text{R}'$  takes place almost quantitatively. Powerful oxidation yields results similar to those obtained with di-substituted dithiourethanes. With weak oxidising agents, the result depends on whether the radicle attached to the nitrogen is alkylic or aromatic; for example,  $\text{NHMe}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\text{Ph}$  is not attacked, whilst  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CS}\cdot\text{SMe}$  yields  $\text{S}_2[\text{C}(\text{SMe})\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}]_2$ . The author concludes that the compounds derived from alkylamines have the constitution  $\text{R}\cdot\text{NH}\cdot\text{CS}\cdot\text{SR}'$ , whilst those derived from aromatic amines have the constitution  $\text{R}\cdot\text{N}\cdot\text{C}(\text{SH})\cdot\text{SR}'$ , the constitution being determined by the more or less acid character of the radicle R. Potassium hydroxide in dilute alcohol dissolves the second but not the first; nitrous acid yields nitroso-derivatives with the first, but simply oxidises the second.

C. H. B.

**New Properties of Urea.** By WILLIAM RAMSDEN (*Proc. Physiol. Soc.*, 1902; *J. Physiol.*, 28, xxiii—xxvi).—The presence of urea dissolved to saturation prevents the heat coagulation of proteids. Various proteids, including gelatin, swell up and dissolve in saturated solutions; the substances formed are acid-albuminate and alkali-albuminate, according to the original reaction of the solution. Urea, up to 10 per cent., increases proteolytic digestion; beyond this strength, it has a retarding influence. Urea is valuable in histology, its action on connective tissues facilitating the separation of a tissue into its individual elements. Urea forms crystalline compounds with fatty acids. Ammonium cyanate and thiocyanate produce many of the effects of urea. Ammonia and ammonium carbonate do not.

W. D. H.

**Some Cases of the Wandering of Oxygen in the Molecule.** By O. LUTZ (*Ber.*, 1902, 35, 2460—2466).—When *l*-bromosuccinic acid is treated with aqueous or methyl alcoholic ammonia (compare Abstr., 1898, i, 127), the ammonium salt of *d*- $\beta$ -malamic acid,  $\text{NH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , is formed, the bromine atom being replaced by a hydroxyl group; the acid crystallises in monoclinic plates melting at  $149^\circ$ , has a sp. gr. 1.577 at  $18^\circ/4^\circ$ , and  $[\alpha]_D + 9.70^\circ$ ; the silver salt crystallises in leaflets. *l*- $\beta$ -Malamic acid is similarly obtained from *d*-chlorosuccinic acid; it melts at  $149^\circ$ , has a sp. gr. 1.576 at  $18^\circ/4^\circ$ , and  $[\alpha]_D - 9.33^\circ$ ; the sodium salt has  $[\alpha]_D - 27.32^\circ$ ; each acid is easily converted into the corresponding malic acid by boiling with alkalis. *r*- $\beta$ -Malamic acid was prepared from *r*-bromosuccinic acid; it melts at  $148^\circ$ , has a sp. gr. 1.526 at  $18^\circ/4^\circ$ , and is less soluble in water than the active acids. Using Curtius and Koch's method (Abstr., 1889, i, 376), *r*- $\beta$ -malamic acid was obtained from aspartic acid and not  $\alpha$ -malamic acid, as these authors supposed.

*l*-β-Malamic acid was also synthesised from malic diamide, by hydrolysis with the calculated quantity of potassium hydroxide or hydrochloric acid. For the acid obtained by both methods, *K* is 0·0286.

K. J. P. O.

**Lead Thiocyanate.** By ROY D. HALL (*J. Amer. Chem. Soc.*, 1902, 24, 570—573).—Pure lead thiocyanate, obtained from lead nitrate and potassium thiocyanate, is not yellow, as stated by Liebig (*Annalen*, 1838, 25, 546), but forms large, transparent, colourless crystals; the product has a yellow colour, however, if the lead nitrate solution contains a salt of bismuth, iron, or mercury. The solubility of lead thiocyanate in water is 3·3 per cent. at 100°, and 0·69 per cent. at 23°.

Basic lead thiocyanate, OH·Pb·CNS, cannot be prepared by boiling the normal salt with water, but is readily obtained by the addition of potassium thiocyanate to a solution of basic lead acetate. It is sparingly soluble in boiling water and separates on cooling in small, acicular crystals.

E. G.

**Sulphur and Nitrogen Derivatives of Carbon Disulphide; Mixed Iminodithiocarbonic Esters.** By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1902, [iii], 27, 585—587).—By acting on a dithiocarbamate of a primary amine with an alkyl haloid, a dithiourethane, R·NH·CS·SR', is formed which can be precipitated with water; this is then dissolved in ether and treated with a slight excess of the second alkyl haloid, when the salt of the mixed base soon begins to crystallise out. *Methyl ethyl methyliminodithiocarbonate*, SMe·C(NMe)·SEt, boils at 205—207°; the corresponding *hydriodide* forms colourless crystals very soluble in water, soluble also in absolute alcohol, melting at 75—77°. The *picrate* forms elongated prisms which melt at 103°; the *platinichloride* melts at 163° with decomposition; the *mercurichloride*, C<sub>5</sub>H<sub>11</sub>NS<sub>2</sub>·HCl<sub>2</sub>·2HgCl<sub>2</sub>, is crystalline and melts at about 83°; the *mercuri-iodide*, C<sub>5</sub>H<sub>11</sub>NS<sub>2</sub>·HI·HgI<sub>2</sub>, crystallises from alcohol in long, yellow needles which melt at 100°.

*Methyl benzyl methyliminodithiocarbonate*, SMe·C(NMe)·S·C<sub>7</sub>H<sub>7</sub>, is a colourless oil which distils at about 300°, at the same time undergoing alteration; the *hydriodide* forms colourless crystals melting at 106°; the *picrate* is also crystalline and melts at 110—112°; the *mercurichloride* and *mercuri-iodide* are oily; the *platinichloride* is a yellowish-orange coloured crystalline powder which melts at 140°.

A. F.

**Synthetical Preparation of Carbon Rings.** By WILLIAM H. PERKIN, jun. (*Ber.*, 1902, 35, 2091—2129).—This lecture contains a review and bibliography of the syntheses of mono- and di-cyclic hydrocarbons and their derivatives.

G. T. M.

**Optically Active Hydrocarbons of the cyclopentene and cyclohexene Series.** By NICOLAI D. ZELINSKY (*Ber.*, 1902, 35, 2488—2494).—1-Methyl-3-cyclopentanone, which has been described by Semmler (*Abstr.*, 1893, i, 129), has the rotation  $[\alpha]_D +135\cdot9^\circ$ , although it is derived from β-methyladipic acid, which is only very

slightly active. The corresponding *alcohol*,  $\text{CHMe} \begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{OH} \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$ , obtained by the reduction of the ketone, boils at  $151.6\text{--}151.8^\circ$ , and has a sp. gr.  $0.9122$  at  $20^\circ/4^\circ$ ,  $n_{21^\circ} = 1.4467$ , and  $[\alpha]_D - 4.89^\circ$ . The alcohol is converted by hydriodic acid into an *iodide*, which boils at  $78\text{--}80^\circ$  under  $32$  mm. pressure and is also slightly levorotatory. When the iodide is heated with alcoholic potash at  $110^\circ$ , it yields

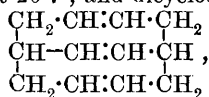
1-methyl- $\Delta^2$ -cyclopentene,  $\text{CHMe} \begin{array}{c} \text{CH} : \text{CH} \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$ , which boils at  $69^\circ$ , has a sp. gr.  $0.7663$  at  $18^\circ/4^\circ$ ,  $n_{18^\circ} = 1.422$ , and  $[\alpha]_D + 59.07^\circ$ . The character of the asymmetric carbon atom of the original ketone is thus preserved throughout the series of changes. The second asymmetric atom present in the alcohol and iodide is of the opposite optical type.

The methylcyclopentene, obtained by the action of crystallised oxalic acid on 1-methyl-3-cyclopentanol, appears to be a mixture of the foregoing compound with the inactive 1-methyl-3-cyclopentene.

Methylcyclohexanol is converted by hydriodic acid into 3-iodo-1-methylcyclohexane, which boils at  $83^\circ$  under  $14$  mm. pressure and is optically active. This compound may be made to yield methylcyclohexene in a variety of ways, and the products differ in optical properties. The hydrocarbon obtained by the action of alcoholic potash boils at  $103\text{--}103.5^\circ$  (corr.), and has a sp. gr.  $0.7937$  at  $27^\circ/4^\circ$ ,  $n_{27^\circ} = 1.4387$ , and  $[\alpha]_D 81.47^\circ$ . This substance seems to be a pure compound, since its properties are not altered by fractional oxidation. The hydrocarbon obtained from the iodide by heating with dimethylaniline boils at  $105.5\text{--}106.5^\circ$  (corr.), and has  $[\alpha]_D 48.29^\circ$ . A less active substance, with  $[\alpha]_D 30.3^\circ$ , is formed by the action of aqueous potassium carbonate on the iodide, and a still less active form, with  $[\alpha]_D 17.78^\circ$ , by the action of oxalic acid on the original alcohol.

It seems possible that the high optical activity of these unsaturated ring compounds may be connected with the stereochemical tension which may be supposed to exist in such molecules. A. H.

**Unsaturated Acids of the Sorbic Acid Series and their Transformation into Cyclic Hydrocarbons.** By OSCAR DOEBNER (*Ber.*, 1902, 35, 2129—2138. Compare this vol., i, 340).—The distillation of an intimate mixture of  $\beta$ -vinylacrylic acid and anhydrous barium hydroxide gives rise to a mixture of two unsaturated hydrocarbons, cycloocta- $\Delta^{1:5}$ -diene,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH} : \text{CH} \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} : \text{CH} \cdot \text{CH}_2 \end{array}$ , a colourless oil boiling at  $50\text{--}52^\circ$  under  $17$  mm. pressure, having an aromatic odour, a sp. gr.  $0.8564$ , and  $n_D 1.49646$  at  $20.7^\circ$ , and dicyclododecatriene,



a yellow oil boiling at  $92\text{--}95^\circ$  under  $17$  mm. pressure, and having a sp. gr.  $0.9764$  and  $n_D 1.5378$  at  $20.7^\circ$ . The formulæ of these substances are confirmed by the cryoscopic determination of the molecular weights in benzene solution.

Sorbic acid, on distillation with barium hydroxide, also yields a



mixture of 3 : 4-dimethylcycloocta- $\Delta^{1:5}$ -diene,  $\begin{array}{c} \text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2 \\ \text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2 \end{array}$ , and trimethyldicyclododecatriene,  $\begin{array}{c} \text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2 \\ \text{CMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH} \\ \text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH} \end{array}$ ; the former is a

colourless oil boiling at 68—71° under 15 mm. pressure, having a sp. gr. 0.8623 and  $n_D$  1.49036 at 13°; it has a faintly aromatic odour and its molecular weight corresponds with the formula  $C_{10}H_{16}$ . The latter hydrocarbon is a yellowish-green, highly refractive oil boiling at 85—87° under 15 mm. pressure; it has a sp. gr. 0.9442 and  $n_D$  1.53321 at 15.5°.

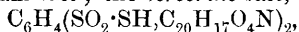
Cinnamenylacrylic acid,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , prepared by heating together cinnamaldehyde, malonic acid, and pyridine, when distilled with barium hydroxide, yields an oily mixture of  $\alpha$ -phenylbuta- $\Delta^{2:7}$ -diene,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2$ , and 3 : 4-diphenylcycloocta- $\Delta^{1:5}$ -diene,  $\begin{array}{c} \text{CHPh}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2 \\ \text{CHPh}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2 \end{array}$ ; the former crystallises from ether in colourless leaflets melting at 25° and boiling at 120—122° under 10 mm. pressure; the latter is a yellowish-green, oily liquid with a blue fluorescence boiling at 204—205° under 10 mm. pressure; it has a sp. gr. 1.018 at 15.3°.

3 : 4-Diphenylcycloocta- $\Delta^{1:5}$ -diene does not combine with bromine and is very slowly attacked by acid or alkaline solutions of permanganate; after 8 days' digestion with the hot oxidising agent, it yields only a trace of benzoic acid. G. T. M.

**Action of Ammonia on  $\alpha\beta$ -Dichlorostyrenes.** By FRANZ KUNCKELL and FRANZ VOSSEN (*Ber.*, 1902, 35, 2294—2295).—2 : 5-Diphenylpyrazine (Staedel and Rügheimer, *Ber.*, 1876, 9, 563) is readily obtained when  $\alpha\beta$ -dichlorostyrene is heated with excess of concentrated ammonia in sealed tubes at 180—200° for 12—18 hours. 2 : 5-Dip-tolylpyrazine, obtained by the action of ammonia on  $\alpha\beta$ -dichloro-*p*-methylstyrene, crystallises in colourless plates melting at 204°.

J. J. S.

**Salts of *m*-Benzenedithiosulphonic Acid.** By JULIUS TROEGER and W. MEINE (*Ber.*, 1902, 35, 2164—2168).—By gradually adding *m*-benzenedisulphonic chloride to a concentrated aqueous solution of potassium disulphide, a solution is obtained which, after filtering and cooling, deposits crystals mainly consisting of potassium *m*-benzenedithiosulphonate; the pure salt can be obtained as a syrup, which gradually solidifies to a hygroscopic mass, by extracting the crude substance with alcohol and evaporating the solution. The silver salt,  $C_6H_4(SO_2\cdot\text{SAG})_2$ , is a white powder which is insoluble in ammonia. The sodium salt resembles the potassium salt; the berberine salt,



is a yellow precipitate; the strychnine salt,  $C_6H_4(SO_2\cdot\text{SH}\cdot C_{21}H_{22}O_2N_2)_2$ , separates from water in white crystals and melts and decomposes at 252°.

On decomposing a solution of potassium *m*-benzenedithiosulphonate

with concentrated hydrochloric acid, sulphur is precipitated, and on evaporating the filtrate a white, insoluble substance,  $C_6H_4S_2O_2$ , separates; this is apparently formed by the decomposition of the disulphinic acid initially produced.

With alcoholic sodium  $\beta$ -thionaphthoxide, *m*-benzenedisulphonic chloride gives  $\beta$ -naphthyl disulphide. W. A. D.

**Triphenylmethyl. V. Carbonium Salts.** By MOSES GOMBERG (*Ber.*, 1902, **35**, 2397—2408).—Determinations of the freezing point of solutions of triphenylchloromethane in benzene gave no evidence of dissociation, whilst boiling point measurements indicated association. When dissolved in liquid sulphur dioxide, however, this series of compounds exhibits an appreciable conductivity which is very marked in the case of triphenylbromomethane. The formation of perhaloids and double salts is also regarded as evidence for the salt-like character of these compounds, whilst the basic character of triphenylcarbinol is deduced from the readiness with which it forms the chloride when treated with hydrogen chloride.

Triphenylmethyl is colourless when solid, but is yellow in solution like the salts of triphenylcarbinol. A theory of 'pseudo-dissociation' with formation of 'pseudo-ions' is advanced to account for this.

T. M. L.

**Bromination and Nitration in the Aromatic Series.** By JAN JOHANNES BLANKSMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 643—647. Compare this vol., i, 442).—*p*-Nitromethylaniline gives trinitrophenol when treated with nitric acid of sp. gr. 1.52. On treatment with 1 mol. of bromine, it gives 2-bromo-4-nitromethylaniline, which melts at 118°, whilst with 2 mols. of bromine it yields 2:6-dibromo-4-nitromethylaniline melting at 113°. The former of these bromine compounds, when treated with nitric acid, gives 2-bromo-4:6-dinitrophenylmethylnitroamine (m. p. 125°), and the latter 2:6-dibromo-4-nitrophenylmethylnitroamine (m. p. 84°).

*o*-Nitromethylaniline likewise gives a trinitrophenylmethylnitroamine when treated with nitric acid, which is converted into 4-bromo-2-nitromethylaniline (m. p. 101°), then into 4:6-dibromo-2-nitromethylaniline (m. p. 100°) by the action of bromine. With nitric acid, the former bromine compound gives 4-bromo-2:6-dinitrophenylmethylnitroamine (m. p. 109°), the latter 2:4-dibromo-6-nitrophenylmethylnitroamine (m. p. 90°).

2:4-Dinitro-6-cyano-1-ethoxybenzene, when treated in alcoholic solution with methylamine or ethylamine, has the ethoxy-group replaced by the methylamino- or ethylamino-group, and by the action of nitric acid on the resulting product the corresponding nitroamine is formed.

The author concludes that: (1) on brominating alkylanilines, bromine enters into the free ortho- and para-positions, whilst the hydrogen atom attached to the nitrogen is not attacked. The same applies to the action of nitric acid, but the amino-hydrogen is simultaneously replaced by the nitro-group. (2) A carboxyl group in the ortho- or para-position is replaced by Br or  $NO_2$  with evolution of carbon

dioxide, and (3) the occupation of the meta-position has no influence on the introduction of Br or NO<sub>2</sub> into the ortho- and para-positions.

The author explains these results as the effect of indirect substitutions. In the bromination or nitration of phenol or aniline, the halogen or NO<sub>2</sub> group first enters the side chain, then shifts to the nucleus. In indirect substitution, the substituting groups always enter the ortho- or para-positions, whilst by direct substitution meta-compounds may be produced. During direct substitution, some groups (CO<sub>2</sub>H, Me, CH<sub>2</sub>·OH, SO<sub>3</sub>H) may be expelled from the ortho- or para-position. J. McC.

**Some Salts of Benzylamine.** By RENÉ DHOMMÉE (*Compt. rend.*, 1902, 134, 1313—1314).—*Benzylamine nitrate*, CH<sub>2</sub>Ph·NH<sub>2</sub>·HNO<sub>3</sub>, is obtained from benzylamine and dilute nitric acid in the form of colourless, hexagonal plates which melt at 136°. One hundred c.c. of water at 19° dissolve 28·6 grams, 100 c.c. of alcohol 20·7 grams.

*Benzylamine sulphate*, CH<sub>2</sub>Ph·NH<sub>2</sub>·H<sub>2</sub>SO<sub>4</sub>, crystallises in colourless needles which melt at 93°. One hundred c.c. of water at 19° dissolve 60·6 grams, 100 c.c. of acetone 32·4 grams, and 100 c.c. of 95 per cent. alcohol 26·0 grams. It is insoluble in ether.

*Benzylamine borate*, CH<sub>2</sub>Ph·NH<sub>2</sub>·2B<sub>2</sub>O<sub>3</sub>·1½H<sub>2</sub>O, forms colourless plates which decompose without fusing at about 200°. At 19°, 100 c.c. of water dissolve 12·2 grams, 100 c.c. of alcohol 1·9 grams, and 100 c.c. of acetone 0·54 gram. It is quite insoluble in ether.

*Benzylamine chromate*, (CH<sub>2</sub>Ph·NH<sub>2</sub>)<sub>2</sub>CrO<sub>3</sub>·2H<sub>2</sub>O, is obtained in golden-yellow plates which do not melt but decompose at 60°. It is insoluble in alcohol and is decomposed by acetone or ether. One hundred c.c. of water at 19° dissolve 4·99 grams.

*Benzylamine oxalate*, (CH<sub>2</sub>Ph·NH<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, forms colourless prisms which melt at 195°. At 15°, 100 c.c. of water dissolve 7·39 grams, 100 c.c. of 95 per cent. alcohol 0·05 gram, and it is insoluble in acetone or ether.

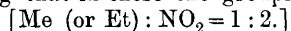
*Benzylamine benzoate*, CH<sub>2</sub>Ph·NH<sub>2</sub>·C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>, crystallises from alcohol in colourless prisms melting at 132—134°. At 19°, 100 c.c. of 95 per cent. alcohol dissolve 8·76 grams, 100 c.c. of ether 0·2 gram, and 100 c.c. of water 0·03 gram. It is decomposed by acetone. J. McC.

**Action of Nitric Acid on Alkylated Amines of *p*-Toluenesulphonic Acid.** By PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 616—618. Compare *Rec. Trav. Chim.*, 1884, 3, 7).—*p*-Toluenesulphonmethyleamide melts at 76—77°, the monoethyl compound at 64°, the *dimethyl* derivative at 76°, and the *diethyl* derivative at 59—60°.

The monomethyl compound, when dissolved in nitric acid of sp. gr. 1·48, gives *nitro-p-toluenesulphonmethylnitroamide* (m. p. 116°) and *p-toluenesulphonmethylnitroamide* (m. p. 60°). With acid of sp. gr. 1·52 only the former is produced. With nitric acid of sp. gr. 1·52, the monoethyl derivative gives *nitro-p-toluenesulphonethylnitroamide* (m. p. 76°); this is decomposed by sulphuric acid, nitrous oxide being evolved and a *nitro-p-toluenesulphonic acid* produced the barium salt of which crystallises with 2 mols. of water.

With nitric acid of sp. gr. 1.48, *p*-toluenesulphondimethylamide yields dimethylamide (?dinitro-dimethylamide) melting at 57°, whilst the diethyl compound with nitric acid of sp. gr. greater than 1.5 gives *nitro-p-toluenesulphonethylnitroamide* (m. p. 76°).

By the action of chlorosulphonic acid on nitrotoluene, a nitrotoluenesulphonic chloride is obtained which with ammonia gives an amine melting at 140°. With potassium nitrotoluenesulphonate, obtained by the action of fuming sulphuric acid on nitrotoluene, phosphorus pentachloride gives a sulphonic chloride from which two amines are produced with ammonia; one of these melts at 141°. *p*-Toluenesulphonic chloride and fuming nitric acid yield a nitro-derivative which can be recrystallised from light petroleum and melts at 45°; the nitro-group enters the ortho-position with reference to the methyl group. It gives an amide melting at 143°. By acting on the 2-nitrotoluene-4-sulphonic chloride with methylamine or ethylamine followed by treatment with nitric acid, the nitro-*p*-toluenesulphonmethyl-nitroamide previously mentioned (or the ethyl derivative) have been obtained, proving that in these the grouping is



J. McC.

**Preparation and Reactions of Derivatives of Formamidines.** By FRANK B. DAINS (*Ber.*, 1902, 35, 2496—2511).—The compound  $\text{NH}\cdot\text{CH}\cdot\text{NH}\cdot\text{CHCl}_2\cdot\text{HCl}$ , obtained by the interaction of hydrogen chloride and cyanide in benzene solution (see Gattermann and Schnitzspahn, *Abstr.*, 1898, i, 546), reacts with 2 mols. of a primary amine, forming formamidine and a disubstituted formamidine,  $\text{NR}\cdot\text{CH}\cdot\text{NHR}$ .

Aniline, *m*- and *p*-nitroanilines, the toluidines,  $\alpha$ -naphthylamine, anisidine, phenetidine, and aminoazobenzene all react with this compound yielding formamidines which have been previously obtained from ethyl orthoformate; *o*-nitroaniline, *p*-aminophenol, and benzidine do not react.

*Di-p-chlorophenylformamidine* crystallises from benzene in white needles, melts at 179°, and forms a *picrate* which crystallises in slender, yellow needles and melts and decomposes at 242°.

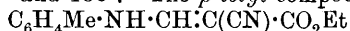
*Di-m-xyllylformamidine* crystallises in white needles and melts at 131°; its *hydrochloride*, *platinichloride*, and *picrate* melt and decompose at 243°, 201°, and 228° respectively. *Di-ψ-cumylformamidine* crystallises in slender, white needles, melts at 160°, and forms a *hydrochloride* melting at 236°. *Di-β-naphthylformamidine* crystallises in slender, white needles and melts at 186°.

Phenylhydrazine and *o*-phenylenediamine react with the compound, forming phenylazophenylhydrazonemethane and benziminoazole respectively.

The disubstituted formamidines react with compounds containing a methylene group, forming compounds of the type  $\text{R}\cdot\text{NH}\cdot\text{CH}\cdot\text{CXY}$ , which have been previously obtained by treating the compounds  $\text{CXY}\cdot\text{CH}\cdot\text{OEt}$  with primary amines. When Y represents a carbethoxy-group, compounds of the type  $\text{R}\cdot\text{NH}\cdot\text{CH}\cdot\text{CX}\cdot\text{CO}\cdot\text{NHR}$  are obtained.

The following new compounds are described. *m-Xylidinomethylene*.

*acetylacetone*,  $C_6H_3Me_2 \cdot NH \cdot CH : C(COMe)_2$ , crystallises in hairy needles melting at  $146^\circ$ . *p-Toluidinomethylenebenzyl cyanide* crystallises in bright brown needles melting at  $135^\circ$ , and the corresponding *m-xylylidino*-compound melts at  $130^\circ$ . The *o-toluidide* of ethyl *o*-toluidinomethylene-malonate,  $C_6H_4Me \cdot NH \cdot CH : C(CO_2Et) \cdot CO \cdot NH \cdot C_6H_4Me$ , melts at  $161^\circ$ , and the corresponding *acid* melts and decomposes at  $161^\circ$ , yielding the *o-toluidide* of *o*-toluidinoacrylic acid. The analogous compound from di-*p*-tolylformamidine melts at  $168^\circ$  and when hydrolysed yields an *acid* melting at  $187^\circ$ ; the analogous compounds from di-*m*-xylyl-, di-*ψ*-cumyl-, di-*p*-chlorophenyl-, di-*p*-anisyl-formamidines melt respectively at  $147^\circ$  (slender, white needles), at  $180^\circ$ , at  $176^\circ$ , and at  $130^\circ$ . The *o-tolyl* compound,  $C_6H_4Me \cdot NH \cdot CH : C(COMe) \cdot CO \cdot NH \cdot C_6H_4Me$  (from di-*o*-tolylformamidine and ethyl acetoacetate), crystallises in needles and melts at  $172^\circ$ , and the analogous *p*-tolyl and *p*-xylyl compounds melt respectively at  $170^\circ$  and  $188^\circ$ . The *p-tolyl* compound,



(from di-*p*-tolylformamidine and ethyl cyanoacetate), melts at  $137^\circ$ , and the analogous *o-tolyl* and *ψ-cumyl* derivatives at  $137$ — $138^\circ$  and  $195^\circ$  respectively.

R. H. P.

#### Action of Phenylcarbimide on the Esters of some Oxy-acids.

II. By EUGÈNE LAMBLING (*Bull. Soc. Chim.*, 1902, [iii], 27, 606—611. Compare this vol., i, 537).—On heating together at  $135$ — $140^\circ$  ethyl *α*-hydroxybutyrate and phenylcarbimide, a reddish-brown oil is obtained, which, however, cannot be distilled without decomposition, and does not crystallise. Its reactions show it to be the *phenylurethane* of ethyl *α*-hydroxybutyrate,  $CH_2Me \cdot C(OH)(CO_2H) \cdot CO \cdot NHPh$ . When saponified with an aqueous solution of sodium hydroxide, the *phenylurethane* of *α*-hydroxybutyric acid is obtained which forms microscopic prisms melting and decomposing at  $116.5$ — $117.5^\circ$ ; it is very soluble in alcohol or ether and soluble in hot benzene or chloroform. The *lactam*, obtained by heating this acid, forms very slender, microscopic needles which melt at  $88^\circ$ ; it is very sparingly soluble in cold water, more soluble in boiling water with partial retransformation into the acid, soluble also in alcohol, ether, benzene, or chloroform.

In a similar manner, the *phenylurethane* of ethyl *α*-hydroxyvalerate has been obtained only in the form of an oil. On boiling this oil with a solution of sodium hydroxide, the alkaline solution deposits on cooling crystals of diphenylcarbimide and of normal *α*-hydroxyvalerianilide. The latter substance, which has also been synthesised by heating aniline with valeric acid, forms pearly scales soluble in boiling water, alcohol, ether, chloroform, or benzene, and melting at  $89$ — $90^\circ$ . On acidifying the alkaline solution, the *phenylurethane* of *α*-hydroxyvaleric acid is obtained in the form of white, prismatic crystals melting at  $78^\circ$ ; it is sparingly soluble in cold water, more soluble in boiling water with partial transformation into its lactam, very soluble in alcohol, ether, chloroform, or benzene, much less so in light petroleum. When boiled with water, the *lactam* is formed together with the anilide; the lactam forms elongated, slender prisms which melt at  $95$ — $96^\circ$  and are soluble in alcohol, ether, chloroform, or benzene, sparingly so in light petroleum.

The *phenylurethane* of *ethyl α-hydroxyisovalerate*, obtained in a manner similar to the preceding compounds, forms a mass of crystalline needles which, however, have not been obtained quite pure. On boiling with a solution of sodium hydroxide, there are formed the *anilide* of *α-hydroxyisovaleric acid* which crystallises in characteristic microscopic octahedra melting at 133°, and the *phenylurethane* of *α-hydroxyisovaleric acid* which crystallises in microscopic, slender needles melting at 111—112°; it is soluble in alcohol, ether, chloroform, or benzene, sparingly so in light petroleum. The corresponding *lactam* forms slender needles which melt at 66—67° and are soluble in alcohol, ether, or benzene.

A. F.

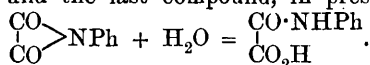
**Cyclic isoNitriles and their Derivatives.** II, III, and IV. By ALEXANDER P. SABANÉEF, E. RAKOWSKY and M. PROSIN (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 398—404, 404—408, 408—410. Compare Abstr., 1901, i, 695).—The authors have investigated the best conditions for preparing acetylenetriphenyltriamine by the action of aniline and potassium hydroxide on acetylene dibromide or tetrabromide or on tribromoethylene. The phenyldicarbylamine also formed in the reaction combines with primary amines, yielding cyclic amidines of the type

$$\begin{array}{c} \text{NHR} \cdot \text{CH} \\ | \\ \text{NHR} \cdot \text{CH} \end{array} > \text{NR}.$$

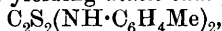
Phenyldicarbylamine combines with sulphur, forming dithio-oxanil,  $\begin{array}{c} \text{CS} \\ | \\ \text{CS} \end{array} > \text{NPh}$ , which is capable of uniting with a molecule of aniline, yielding dithio-oxanilide,  $\text{NPh} \cdot \text{CS} \cdot \text{CS} \cdot \text{NPh}$ , formerly obtained by Wallach (Abstr., 1880, 556). Phenyldicarbylamine is also readily

oxidised according to the equation:  $\begin{array}{c} \text{C} \\ ||| \\ \text{O} \end{array} > \text{NPh} + \text{O}_2 = \begin{array}{c} \text{CO} \\ | \\ \text{CO} \end{array} > \text{NPh};$

and the last compound, in presence of water, yields oxanilic acid:



When a mixture of *p*-toluidine with acetylene tetrabromide is treated with alcoholic potassium hydroxide, *p*-tolylldicarbylamine is first formed, and this combines with *p*-toluidine, yielding a cyclic amidine of the constitution  $\begin{array}{c} \text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CH} \\ | \\ \text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CH} \end{array} > \text{N} \cdot \text{C}_6\text{H}_4\text{Me}$ ; this compound separates from alcohol in snow-white flocks which darken at 132° and melt at about 145°. It dissolves readily in acids, forming salts: the *hydrochloride*,  $\text{C}_{23}\text{H}_{25}\text{N}_3 \cdot 2\text{HCl}$ , and the *platinichloride*,  $\text{C}_{23}\text{H}_{25}\text{N}_3 \cdot \text{H}_2\text{PtCl}_6$ , were prepared and analysed. *p*-Tolylldicarbylamine also unites with sulphur, yielding *dithio-oxal-p-toluidide*,

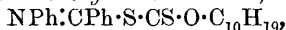


which crystallises from alcohol in golden-yellow, shining plates melting at 150°.

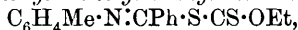
T. H. P.

**Iminoxanthides, a New Class of Coloured Organic Compounds.** By L. TSCHUGAEFF (*Ber.*, 1902, 35, 2470—2473).—Aromatic iminochlorides of the type  $\text{R}'\cdot\text{CCl}:\text{NR}''$  react with the sodium

salts of the xanthic esters,  $R''O\cdot CS\cdot SNa$ , to form iminoxanthides,  $NR''\cdot CR'\cdot S\cdot CS\cdot OR''$ . These compounds are coloured various shades of red, but are not dyes, the chromophoric group being probably  $[ \cdot CS\cdot S\cdot C\cdot N ]$ . They are neutral substances without any basic properties, and by hydrolysis are resolved into the corresponding alcohol, acid and base. The following have been prepared:—1:2-*Diphenyl-3-ethyl-iminoxanthide*,  $NPh\cdot CPh\cdot S\cdot CS\cdot OEt$ , forms garnet-red prisms melting  $98-98.5^\circ$ , and yields aniline, benzoic acid, and ethyl alcohol on hydrolysis. 1:2-*Diphenyl-3-1-menthyliminoxanthide*,



forms orange-red, matted needles melting at  $105-106^\circ$ . 1:2-*Diphenyl-3-bornyliminoxanthide*,  $NPh\cdot CPh\cdot S\cdot CS\cdot O\cdot C_{10}H_{17}$ , was prepared in both its optically isomeric forms; these are identical in appearance and melting point, and crystallise extremely well in bright red prisms melting at  $87-88^\circ$ . The inactive racemic form separates in small, red crystals and melts at  $89-90^\circ$ . 1:2-*Diphenyl-3-fenchyliminoxanthide*, forms small, brownish-red crystals melting at  $84-85^\circ$ . This compound is isomeric with bornyliminoxanthide, but differs from it remarkably in colour. 1:2-*Diphenyl-3-benzyliminoxanthide*,  $NPh\cdot CPh\cdot S\cdot CS\cdot O\cdot C_7H_7$ , forms long, matted, ponceau-red needles melting at  $72-73^\circ$ . 1-*Phenyl-2-o-tolyl-3-ethyliminoxanthide*,



crystallises in scarlet prisms melting at  $76-77^\circ$ . 1-*Phenyl-2-ψ-cumyl-iminoxanthide*,  $C_6H_2Me_3\cdot N\cdot CPh\cdot S\cdot CS\cdot OEt$ , forms dark red tablets melting at  $96-97^\circ$ .

The iminoxanthides of the terpene series are the first examples, other than salts, of optically active substances which are strongly coloured.

A. H.

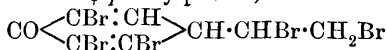
**The Phenols from Shale Oil.** By THOMAS GRAY (*J. Soc. Chem. Ind.*, 1902, 21, 845-847).—"Green naphtha" creosote from shale oil contains 5-6 per cent. of phenol, and 12-15 per cent. of *o*-cresol, but the bulk of the mixture is composed of *m*-cresol and xylenols, which seem to be present in approximately equal quantity, namely, 30-35 per cent.; of the xylenols, the isomerides having the configuration  $[Me_2\cdot OH = 1:2:4 \text{ and } = 1:3:5]$  have been identified. Sixteen per cent. of the total phenols are present in the fraction boiling above  $230^\circ$ . Cresol and *p*-cresol seem to be absent, and guaiacol is present in very small quantity.

L. DE K.

**Action of Bromine and Chlorine on Phenols, Substitution Products, ψ-Bromides, and ψ-Chlorides.** By THEODOR ZINCKE, O. SIEBERT, and H. REINBACH (*Annalen*, 1902, 322, 174-238. Compare this vol., i, 282).—*Tribromo-p-ethylphenol*,  $C_6H_4EtBr_3\cdot OH$ , readily obtained by adding bromine to a chloroform solution of *p*-ethylphenol in the presence of iron wire, crystallises in flattened, silky needles melting at  $54-55^\circ$ ; it is readily soluble in dilute sodium hydroxide solution and yields an *acetyl* derivative separating in lustrous, monoclinic crystals melting at  $70^\circ$ . *Tetrabromo-p-ethylphenol*,  $C_6H_4EtBr_4\cdot OH$ , although obtained by Fittig and Kiesow by adding bromine to powdered *p*-ethylphenol, is prepared with greater certainty by

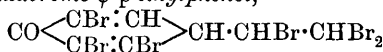
operating in chloroform solution in the presence of iron wire; if aluminium is employed, no solvent is required; it crystallises in white needles and melts at 109—110°; its *acetyl* derivative crystallises from glacial acetic acid and melts at 133—134°.

$\alpha\beta$ -2 : 3 : 5-Pentabromo- $\psi$ -*p*-ethylphenol,



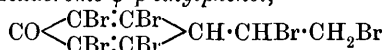
or  $\text{OH} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CHBr} \cdot \text{CH}_2\text{Br}$ , is conveniently prepared by heating tribromo-*p*-ethylphenol with the theoretical amount of bromine under pressure at 100°; it crystallises from a mixture of light petroleum and benzene either in spherical aggregates of needles melting at 129°, or in prisms melting at 131°. This substance may also be prepared either by adding bromine to tribromo-*p*-vinylphenol, or hydrogen bromide to tribromo- $\beta$ -bromo-*p*-vinylphenol; it does not behave like a phenol, and dissolves only slowly in solutions of the alkali hydroxides with decomposition.

$\alpha\beta\beta$ -2 : 3 : 5-Hexabromo- $\psi$ -*p*-ethylphenol,



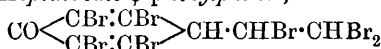
or  $\text{OH} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CHBr} \cdot \text{CHBr}_2$ , produced either by heating the pentabromide or the tribromo-compound with bromine at 100°, or by adding the halogen to 2 : 3 : 5- $\beta$ -tetrabromo-*p*-vinylphenol, crystallises in needles melting at 131—132°; it slowly dissolves in solutions of the alkali hydroxides, becoming soluble more rapidly in the presence of acetone; with concentrated sulphuric acid, it develops a deep red coloration.

$\alpha\beta\beta$ -2 : 3 : 5 : 6-Hexabromo- $\psi$ -*p*-ethylphenol,



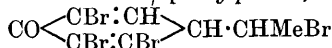
or  $\text{OH} \cdot \text{C}_6\text{HBr}_4 \cdot \text{CHBr} \cdot \text{CH}_2\text{Br}$ , obtained by heating tetrabromo-*p*-ethylphenol with the theoretical amount of bromine at 120—160°, separates from a mixture of benzene and light petroleum in crystals melting at 179°; it dissolves in alkali hydroxide solutions, but only in the presence of acetone.

$\alpha\beta\beta$ -2 : 3 : 5 : 6-Heptabromo- $\psi$ -*p*-ethylphenol,



or  $\text{OH} \cdot \text{C}_6\text{HBr}_4 \cdot \text{CHBr} \cdot \text{CHBr}_2$ , formed from tetrabromo-*p*-ethylphenol by the action of excess of bromine at 130—140°, crystallises in lustrous rhombohedra and melts at 174°. The substance is readily converted into an ethylidenequinone containing six bromine atoms; zinc and hydrogen bromide in ether reduce it to bromo-*p*-vinyltetrabromophenol.

2 : 3 : 5-Tribromo-*p*-vinylphenol,  $\text{OH} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CH} \cdot \text{CH}_2$ , obtained by reducing  $\alpha\beta$ -2 : 3 : 5-pentabromo- $\psi$ -*p*-ethylphenol with granulated zinc and hydrogen bromide, crystallises from light petroleum or 80 per cent. acetic acid in colourless leaflets or needles melting at 93—94°; the *acetyl* compound separates in nodular aggregates melting at 86—87°.  $\alpha$ -2 : 3 : 5-Tetrabromo- $\psi$ -*p*-ethylphenol,



or  $\text{OH} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CHMeBr}$ , formed by adding hydrogen bromide to the vinyl compound, crystallises in plates and melts at 87°. The addition of bromine leads to the regeneration of the pentabromo- $\psi$ -phenol.



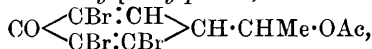
$\beta$ -2 : 3 : 5-Tetrabromo-p-vinylphenol,  $\text{OH} \cdot \text{C}_6\text{HBr}_2 \cdot \text{CH} : \text{CHBr}$ , prepared from the hexabromide, crystallises from a mixture of benzene and petroleum in colourless needles and melts at  $167^\circ$ ; the *acetyl* compound forms white leaflets and melts at  $155^\circ$ ; it yields the original hexabromide on adding bromine, and the addition of hydrogen bromide leads to the production of the pentabromo-compound melting at  $129$ — $131^\circ$ .

$\beta$ -2 : 3 : 5 : 6-Pentabromo-p-vinylphenol,  $\text{OH} \cdot \text{C}_6\text{HBr}_4 \cdot \text{CH} : \text{CHBr}$ , prepared from the heptabromo-compound, crystallises in needles and melts at  $170$ — $171^\circ$ ; its *sodium* salt is sparingly soluble, and its *acetyl* compound melts at  $172^\circ$ ; the heptabromide is regenerated by the addition of bromine.

2 : 3 : 5-Tribromo- $\alpha$ -hydroxy-p-ethylphenol,  $\text{OH} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CHMe} \cdot \text{OH}$ , obtained by heating the corresponding tetrabromo-derivative with dilute acetone, crystallises in needles melting at  $117$ — $118^\circ$ ; it dissolves in the alkali hydroxides without decomposition and is soluble in the ordinary organic solvents; its *diacetyl* derivative crystallises from glacial acetic acid in colourless needles and melts at  $71^\circ$ .

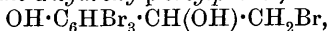
2 : 3 : 5-Tribromo- $\alpha$ -methoxy-p-ethylphenol,  $\text{OH} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CHMe} \cdot \text{OMe}$ , produced by heating the tetrabromo-compound with methyl alcohol separates from light petroleum in spherical aggregates melting at  $97^\circ$ .

2 : 3 : 5-Tribromo- $\alpha$ -acetoxy-p-ethylphenol,

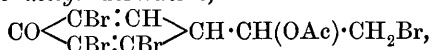


prepared by heating the tetrabromide with glacial acetic acid and sodium acetate, forms white crystals melting at  $186$ — $187^\circ$ ; it dissolves in the ordinary organic solvents, but is decomposed by alkali hydroxide solutions.

$\beta$ -2 : 3 : 5-Tetrabromo- $\alpha$ -hydroxy-p-ethylphenol,



obtained from the pentabromide by the action of dilute acetone, crystallises in plates and melts at  $147$ — $148^\circ$ ; it is decomposed by alkali hydroxides; the *acetyl* derivative,



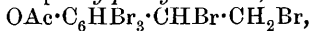
or  $\text{OH} \cdot \text{C}_6\text{HBrCH}(\text{OAc})\text{CH}_2\text{Br}$ , prepared by boiling the pentabromide with glacial acetic acid and sodium acetate; it melts at  $164$ — $165^\circ$  and yields the *diacetyl* compound on treatment with acetic anhydride; this substance separates from light petroleum in acicular crystals melting at  $110$ — $111^\circ$ .

$\beta$ -2 : 3 : 5-Tetrabromo- $\alpha$ -methoxy-p-ethylphenol,



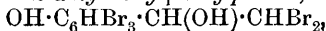
resulting from the interaction of methyl alcohol and the pentabromide, crystallises in thick needles and melts at  $133$ — $134^\circ$ ; its *acetyl* derivative crystallises in yellow needles and melts at  $90$ — $91^\circ$ .

$\alpha\beta$ -2 : 3 : 5-Pentabromo-p-ethylphenyl acetate,

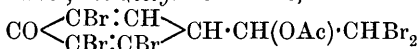


prepared by heating the pentabromide with acetic anhydride, separates in monoclinic crystals and melts at  $143$ — $144^\circ$ .

$\beta\beta$ -2 : 3 : 5-Pentabromo- $\alpha$ -hydroxy-p-ethylphenol,

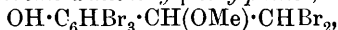


obtained from the hexabromide, forms lustrous, monoclinic crystals melting at 125—126; its *acetyl* derivative,



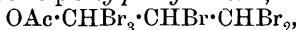
or  $\text{OH}\cdot\text{C}_6\text{HBr}_3\cdot\text{CH}(\text{OAc})\cdot\text{CHBr}_2$ , also separates in monoclinic crystals melting at 128—129; its *diacetyl* compound crystallises in needles and melts at 131—132°.

$\beta\beta$ -2 : 3 : 5-*Pentabromo- $\alpha$ -methoxy-*p*-ethylphenol*,



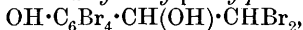
separates in white, spherical aggregates and its *acetyl* derivative in white needles, they melt at 120° and 150—151° respectively.

$\alpha\beta\beta$ -2 : 3 : 5-*Hexabromo-*p*-ethylphenyl acetate*,



prepared by heating the hexabromide with acetic anhydride, crystallises in plates and melts at 116—117°.

$\beta\beta$ -2 : 3 : 5 : 6-*Hexabromo- $\alpha$ -hydroxy-*p*-ethylphenol*,

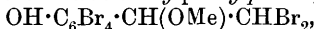


obtained by warming the heptabromide with dilute acetone, crystallises in colourless needles melting at 156—157°; the *acetyl* derivative,



is produced by heating the heptabromide with acetic anhydride, the *diacetyl* compound is the result of more prolonged action in the presence of sodium acetate; they separate in colourless crystals melting respectively at 177—178° and 124—125°.

$\beta\beta$ -2 : 3 : 5 : 6-*Hexabromo- $\alpha$ -methoxy-*p*-ethylphenol*,

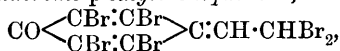


obtained by boiling the heptabromide with methyl alcohol, separates in rhombohedral crystals and melts at 109—110°.

$\alpha\beta\beta$ -2 : 3 : 5 : 6-*Heptabromo-*p*-ethylphenol*,  $\text{OAc}\cdot\text{C}_6\text{Br}_4\cdot\text{CHBr}\cdot\text{CHBr}_2$ ,

prepared by warming the heptabromide with acetic anhydride for a short time, separates from glacial acetic acid in lustrous crystals melting at 129—130°.

$\beta\beta$ -2 : 3 : 5 : 6-*Hexabromo-*p*-ethylidenequinone*,

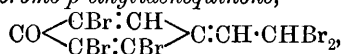


produced by shaking a 10 per cent. sodium acetate solution with the heptabromide dissolved in petroleum and dry ether, is a deep yellow, crystalline powder sintering at 180° and melting at 230—235°; when treated with solvents, it readily decomposes, yielding a white, amorphous substance. It readily forms additive products, thus on treatment with water, methyl alcohol, or acetic anhydride it yields  $\beta\beta$ -2 : 3 : 5 : 6-hexabromo- $\alpha$ -hydroxy-*p*-ethylphenol,  $\beta\beta$ -2 : 3 : 5 : 6-hexabromo- $\alpha$ -methoxy-*p*-ethylphenol, and  $\beta\beta$ -2 : 3 : 5 : 6-hexabromo- $\alpha$ -acetoxy-*p*-ethylphenyl acetate respectively. The heptabromide is regenerated by the addition of hydrogen bromide, and  $\beta$ -2 : 3 : 5 : 6-pentabromo-*p*-vinylphenol results from the action of zinc and an ethereal hydrogen bromide solution.

The white, amorphous *compound*,  $\text{C}_8\text{H}_2\text{Br}_6\text{O}$ , sinters at 150—155° and melts at 165°; it is far less reactive than the quinone, but nevertheless slowly forms additive products with acetic anhydride and water which are identical with those obtained from the quinone.

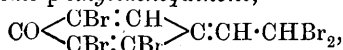
The heptabromide yields a white, insoluble product when its ethereal solution is shaken with anhydrous sodium acetate; this compound,  $C_8H_2Br_6O$ , is an amorphous powder decomposing at about  $200^\circ$ .

$\beta\beta$ -2 : 3 : 5-Pentabromo-*p*-ethylidenequinone,



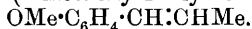
obtained from the hexabromide, is a yellow, granular powder, sintering at  $100^\circ$  and decomposing at  $180^\circ$ ; it is accompanied by a white, insoluble product into which it is readily converted by the action of solvents. The quinone readily forms addition products, and with aqueous acetone, methyl alcohol, and acetic acid gives rise to the corresponding  $\alpha$ -hydroxy-,  $\alpha$ -methoxy-, and  $\alpha$ -acetoxy-derivatives of  $\beta\beta$ -2 : 3 : 5-pentabromo-*p*-ethylphenol. Hydrogen bromide alone regenerates the hexabromide and in the presence of zinc,  $\beta$ -2 : 3 : 5-tetrabromo-*p*-vinylphenol is produced. The insoluble quinonoid compound also forms the same additive products with hydrogen bromide and methyl alcohol. With aqueous acetone and acetic acid, it yields compounds melting respectively at  $135$ — $136^\circ$  and  $134$ — $135^\circ$ ; the former has the same composition as the quinone, namely,  $C_8H_3Br_5O$ , but dissolves in alkali hydroxide solutions, the latter is insoluble in these reagents.

$\beta$ -2 : 3 : 5-Tetrabromo-*p*-ethylidenequinone,



obtained from the pentabromide only in very small amount, is a yellow, amorphous powder; it is accompanied by a large quantity of white, insoluble product. The quinone reacts with hydrogen bromide, regenerating the pentabromide, and when treated with methyl alcohol and acetic acid furnishes the corresponding  $\alpha$ -methoxy- and  $\alpha$ -acetoxy-derivatives of  $\beta$ -2 : 3 : 5-tetrabromo-*p*-ethylphenol. G. T. M.

**Synthesis of Unsaturated Phenol-Ethers.** By AUGUST KLAGES (*Ber.*, 1902, 35, 2262—2267).—Propionylanisole (Gattermann, Erhardt, and Maisch, *Abstr.*, 1890, 963) which can be prepared in quantity by the action of aluminium chloride on propionyl chloride and anisole, boils at  $148^\circ$  under 14 mm. pressure, and solidifies to colourless crystals. 4-Methoxy-1- $\alpha$ -hydroxypropylbenzene,  $OMe \cdot C_6H_4 \cdot CH_2 \cdot OH$ , is a colourless, viscous oil, boils at  $141$ — $142^\circ$  under 16 mm. pressure and has a sp. gr. 1.042 at  $17^\circ$ . The phenylurethane  $C_{17}H_{19}O_3N$ , crystallises from a mixture of alcohol and light petroleum in stout tablets and melts at  $74^\circ$ . The acetate,  $C_{12}H_{15}O_3$ , boils at  $156^\circ$  under 20 mm. pressure and has a sp. gr. 1.005 at  $16^\circ$ . By heating with pyridine, the acetate was converted into anethole (4-methoxy-1-allylbenzene),



Propionylphenetole,  $OEt \cdot C_6H_4 \cdot COEt$ , boils at  $153$ — $154^\circ$  under 13 mm. pressure and solidifies on cooling. 4-Ethoxy-1- $\alpha$ -hydroxypropylbenzene,  $OEt \cdot C_6H_4 \cdot CH_2 \cdot OH$ , is a colourless, viscous oil, of a sweet, burning taste, slightly soluble in water, boils at  $144.5$ — $145.5^\circ$  under 10 mm. and at  $150^\circ$  under 15 mm. pressure, and has a sp. gr. 1.0222 at  $22/4^\circ$ . The phenylurethane,  $C_{18}H_{21}O_3N$ , forms minute, felted needles, and melts at  $82^\circ$ . The acetate,  $C_{13}H_{18}O_3$ , is a water-white, odourless

liquid and boils at  $161^{\circ}$  under 17 mm. pressure. *Anæthole* (4-ethoxy-1-allylbenzene),  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CHMe}$ , crystallises from alcohol in colourless glistening flakes, is volatile with steam, and boils at  $134\text{--}136^{\circ}$  under 18 mm. and at  $242^{\circ}$  under atmospheric pressure. The *nitrosochloride*,  $\text{C}_{11}\text{H}_{14}\text{O}\cdot\text{ONCl}$ , separates in colourless, glistening crystals and melts at  $115\cdot5^{\circ}$ .

*p-Propionylisobutoxybenzene*,  $\text{C}_4\text{H}_9\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{COEt}$ , crystallises from alcohol in glistening tablets, melts at  $52^{\circ}$ , and boils at  $172\text{--}174^{\circ}$  under 14 mm. pressure. The *oxime*,  $\text{C}_{13}\text{H}_{19}\text{O}_2\text{N}$ , separates from absolute alcohol in colourless crystals and melts at  $49^{\circ}$ . 4-iso*Butoxy-1- $\alpha$ -hydroxypropylbenzene*,  $\text{C}_4\text{H}_9\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CHEt}\cdot\text{OH}$ , is a colourless, oily liquid of faint odour and burning taste and boils at  $164\text{--}165^{\circ}$  under 14 mm. pressure. The *phenylurethane*,  $\text{C}_{20}\text{H}_{25}\text{O}_3\text{N}$ , separates from alcohol in colourless needles and melts at  $57^{\circ}$ .

*Butyrylphenetole*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{COPr}^a$ , boils at  $173\text{--}174^{\circ}$  under 23 mm. pressure, has a faint odour, and solidifies to colourless crystals. 4-*Ethoxy-1- $\alpha$ -hydroxybutylbenzene*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{CHPr}^a\cdot\text{OH}$ , boils at  $164\text{--}166^{\circ}$  under 23 mm. pressure, melts at about  $22^{\circ}$ , and has a sp. gr. 1.003 at  $19^{\circ}$ . *Butenylphenetole*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CHEt}$ , is a colourless oil of pleasant aromatic odour, boils at  $123\text{--}124^{\circ}$  under 12 mm. pressure and has a sp. gr. 0.9452 at  $20^{\circ}$ . T. M. L.

**Halogen Derivatives of Dimethyldihydroresorcin.** By DANIEL VORLÄNDER and M. KOHLMANN (*Annalen*, 1902, 322, 239—259. Compare Crossley and Le Sueur, *Trans.*, 1902, 81, 821).—*Chlorodimethyldihydroresorcin*,  $\text{CMe}_2\left\langle\begin{array}{c} \text{CH}_2\text{---CO} \\ \text{CH}_2\cdot\text{C}(\text{OH}) \end{array}\right\rangle\text{CCl}$ , produced together with dimethylglutaric acid by the action of alkali hypochlorites on dimethyldihydroresorcin, crystallises from alcohol in leaflets containing  $1\text{H}_2\text{O}$ . The water of crystallisation is removed by leaving the substance in a desiccator; the anhydrous compound melts at  $161^{\circ}$ .

*Bromodimethyldihydroresorcin*,  $\text{CMe}_2\left\langle\begin{array}{c} \text{CH}_2\text{---CO} \\ \text{CH}_2\cdot\text{C}(\text{OH}) \end{array}\right\rangle\text{CBr}$ , prepared by treating dimethyldihydroresorcin either with bromine dissolved in chloroform or an alkaline solution of a hypobromite, crystallises in leaflets also containing  $1\text{H}_2\text{O}$ ; the anhydrous substance melts at  $175^{\circ}$  and not at  $143\text{--}144^{\circ}$ . This compound, when treated with excess of hypobromite, is oxidised, yielding a mixture of carbon tetrabromide and  $\beta\beta$ -dimethylglutaric acid.

These two monohalogen derivatives behave as monobasic acids.

The *anilide*,  $\text{CMe}_2\left\langle\begin{array}{c} \text{CH}_2\text{---CO} \\ \text{CH}_2\cdot\text{C}(\text{NHPh}) \end{array}\right\rangle\text{CBr}$ , produced by heating this substance with aniline, crystallises from glacial acetic acid and melts at  $159\text{--}160^{\circ}$ . The *methyl ester*,  $\text{CMe}_2\left\langle\begin{array}{c} \text{CH}_2\text{---CO} \\ \text{CH}_2\cdot\text{C}(\text{OMe}) \end{array}\right\rangle\text{CBr}$ , obtained by boiling the hydroxy-compound with methyl alcohol containing sulphuric acid, crystallises from methyl alcohol and melts at  $104^{\circ}$ .

The *methyl ester* of dimethyldihydroresorcin, prepared in a similar manner, is a colourless oil boiling at  $132\text{--}134^{\circ}$  under 15 mm. pressure; when treated with bromine in chloroform solution, it yields bromodimethyldihydroresorcinol and a white, indeterminate substance.

*Iododimethyldihydroresorcin*,  $\text{CMe}_2 \begin{smallmatrix} \text{CH}_2 \text{---} \text{CO} \\ \text{CH}_2 \cdot \text{C}(\text{OH}) \end{smallmatrix} \text{I}$ , produced by mixing an ethereal solution of iodine with an alcoholic solution of the sodium derivative of dimethyldihydroresorcin, crystallises from dilute methyl alcohol in slender needles partially decomposing at  $135^\circ$  and melting at  $160\text{--}162^\circ$ . These halogen derivatives of dimethyldihydroresorcin are very stable towards boiling sodium hydroxide solutions, the chloro- and bromo-compounds remain practically unchanged, whilst the iodo-derivative is only slightly attacked.

*Dichlorodimethyldihydroresorcin*,  $\text{CMe}_2 \begin{smallmatrix} \text{CH}_2 \text{---} \text{CO} \\ \text{CH}_2 \cdot \text{C}(\text{OCl}) \end{smallmatrix} \text{CCl}$ , results from the action of dry chlorine on dimethyldihydroresorcin dissolved in chloroform, crystallises in lustrous needles and melts at  $112^\circ$ ; it dissolves in the ordinary organic solvents, but is insoluble in cold solutions of alkali hydroxides; when, however, the mixture is warmed, the dichloride is decomposed, and the solution then contains an alkali hypochlorite. Stannous chloride reduces the dichloride, giving rise to chlorodimethyldihydroresorcin.

*Dibromodimethyldihydroresorcin*,  $\text{CMe}_2 \begin{smallmatrix} \text{CH}_2 \text{---} \text{CO} \\ \text{CH}_2 \cdot \text{C}(\text{OBr}) \end{smallmatrix} \text{CBr}$ , also prepared by the action of the halogen in chloroform solution, crystallises from dilute methyl alcohol in needles melting at  $144^\circ$ . With excess of dimethyldihydroresorcin, this reaction leads to the formation of the monobromide accompanied by tarry products. The dibromide is insoluble in solutions of the alkali carbonates or hydroxides, but when shaken up with the latter it slowly decomposes, and the solution is found to contain bromoform, carbon tetrabromide, and an alkali hypobromite; this reaction occurs more rapidly on warming.

These disubstituted halogen derivatives both liberate iodine from a solution of potassium iodide; this action does not occur with the mono-halogen compounds.

$\beta\beta$ -Dimethylglutaric acid can be very readily prepared by treating an alkaline solution of dimethyldihydroresorcin at  $40\text{--}50^\circ$  with an emulsion of chloride of lime.

G. T. M.

**Styrene.** By AUGUST KLAGES [in part with EMIL FANTO and HERMANN PIERSTORFF] (*Ber.*, 1902, 35, 2245—2262).—1-Methyl-4- $\alpha$ -hydroxyethylbenzene,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHMe}\cdot\text{OH}$ , prepared by reducing *p*-acetyltoluene with sodium and ethyl alcohol, is a colourless, viscous oil, boils at  $120^\circ$  under 19 mm. pressure, and has a sp. gr. 0.9668 at  $15.5^\circ/4^\circ$ . The phenylurethane,  $\text{C}_{16}\text{H}_{17}\text{O}_2\text{N}$ , is a crystalline compound, melts at  $95\text{--}96^\circ$ , and dissolves readily in benzene. The chloride,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHMeCl}$ , is a pale, yellowish oil which liberates hydrogen chloride when heated. *p*-Methylstyrene,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}\cdot\text{CH}_2$ , prepared by heating the chloride with pyridine, is a colourless, mobile oil with an odour suggestive of turpentine, boils at  $60^\circ$  under 12 mm. pressure, and has a sp. gr. 0.8974 at  $18^\circ/4^\circ$ . A nitrosochloride could not be obtained.

1:3-Dimethyl-4- $\alpha$ -hydroxyethylbenzene,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CHMe}\cdot\text{OH}$ , is a colourless, viscous oil of sharp odour, boils at  $118^\circ$  under 12 mm. pressure, and has a sp. gr. 0.9863 at  $13^\circ/4^\circ$ . The phenylurethane,  $\text{C}_{17}\text{H}_{19}\text{O}_2\text{N}$ , separates from light petroleum in colourless needles and

melts at  $105^{\circ}$ . The *chloride* forms an additive product,  $C_{15}H_{18}NCl \cdot H_2O$ , with pyridine, which separates in needles from a mixture of alcohol and ether and melts at  $153^{\circ}$ ; the *platinichloride*,  $(C_{15}H_{17}N)_2 \cdot H_2PtCl_6$ , separates from hot water in yellowish needles and melts at  $198^{\circ}$ ; the *aurichloride*,  $C_{15}H_{17}N \cdot HAuCl_4$ , crystallises from alcohol in well-formed, golden-yellow needles, melts at  $113^{\circ}$ , and is more soluble than the platinichloride. When heated with water at  $100^{\circ}$ , the additive product decomposes into pyridine hydrochloride and dimethylstyrene, but when heated with water at  $120^{\circ}$  it gives a polymeride,  $(C_{10}H_{12})_8$ , resembling Canada balsam.

The *oxime* of *p*-acetyl ethylbenzene (Klages and Lickroth, Abstr., 1899, i, 599) crystallises from alcohol in stout, tabular crystals and melts at  $82-83^{\circ}$ .

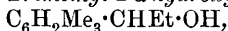
1-Ethyl-4- $\alpha$ -hydroxyethylbenzene,  $C_6H_4Et \cdot CHMe \cdot OH$ , is a colourless, viscous oil with a faint odour, boils at  $119.5^{\circ}$  under 14 mm. pressure, and has a sp. gr. 0.9737 at  $18^{\circ}/4^{\circ}$ . The *phenylurethane*,  $C_{17}H_{19}O_2N$ , crystallises from alcohol in needles and melts at  $72-73^{\circ}$ . The *chloride*,  $C_6H_4Et \cdot CHMeCl$ , is a colourless, mobile oil and boils at  $112.5-113^{\circ}$  under 18 mm. pressure. *p*-Ethylstyrene,  $C_6H_4Et \cdot CH:CH_2$ , is a colourless, mobile oil with an odour suggestive of turpentine, boils at  $86^{\circ}$  under 20 mm. pressure, and has a sp. gr. 0.9074 at  $13^{\circ}/4^{\circ}$ ; after some weeks, it changes to an odourless, stiff, transparent resin; a nitrosochloride could not be obtained.

Vinylmesitylene (2 : 4 : 6-trimethylstyrene) (Klages and Allendorff, Abstr., 1898, i, 433) can be prepared by a similar method; it does not polymerise after keeping for a year, and does not yield a nitrosochloride.

Allylbenzene,  $C_6H_5 \cdot CH:CHMe$ , boils at  $74^{\circ}$  under 13 mm. pressure and has a sp. gr. 0.9083 at  $19^{\circ}/4^{\circ}$ .

1-Methyl-4- $\alpha$ -hydroxypropylbenzene,  $C_6H_4Me \cdot CHEt \cdot OH$ , boils at  $118-120^{\circ}$  under 23 mm., and at  $223-226^{\circ}$  under atmospheric pressure, has a sp. gr. 0.966 at  $14.5^{\circ}$ , and solidifies on ice to colourless crystals melting at  $15^{\circ}$ . The *acetate*,  $C_{12}H_{16}O_2$ , boils at  $130^{\circ}$  under 25 mm. pressure and has a sp. gr. 0.989 at  $14^{\circ}$ . The *phenylurethane*,  $C_{17}H_{19}O_2N$ , separates from light petroleum in colourless crystals and melts at  $86-88^{\circ}$ . The *chloride*,  $C_6H_4Me \cdot CHEt \cdot Cl$ , is largely decomposed with liberation of hydrogen chloride when distilled in a vacuum. *p*-Methylallylbenzene,  $C_6H_4Me \cdot CH:CHMe$ , is a colourless, mobile oil with an odour resembling that of styrene, and boils at  $92-93^{\circ}$  under 20 mm. pressure. The *nitrosochloride*,  $C_{10}H_{12}ONCl$ , is readily formed and is very characteristic. It separates in colourless needles and melts at  $135^{\circ}$ . The hydrocarbon is perhaps identical with Errera's allyltoluene (Abstr., 1885, 772).

Propionylmesitylene,  $C_6H_2Me_3 \cdot COEt$ , is a yellowish, mobile liquid of sharp odour, boils at  $125^{\circ}$  under 13 mm. pressure, and has the sp. gr. 0.962 at  $24^{\circ}/4^{\circ}$ . 1 : 3 : 5-Trimethyl-2- $\alpha$ -hydroxypropylbenzene,



is a viscous, colourless oil, boils at  $172^{\circ}$  under 14 mm. pressure, and has a sp. gr. 0.9705 at  $24^{\circ}/4^{\circ}$ . The *phenylurethane*,  $C_{19}H_{23}O_2N$ , crystallises from alcohol in colourless needles and melts at  $141^{\circ}$ . The *chloride* was converted directly, by boiling with pyridine, into allylmesitylene,  $C_6H_2Me_3 \cdot CH:CHMe$ , a colourless, mobile liquid of turpentine-like

odour, which boils at  $103^{\circ}$  under 13 mm. pressure, has a sp. gr. 0.9003 at  $17.5^{\circ}/4^{\circ}$ , and does not polymerise on keeping. The *nitrosochloride*,  $C_{12}H_{16}ONCl$ , separates in minute crystals and melts at  $146.5^{\circ}$ .

4-Butyryl-1:3-dimethylbenzene,  $C_6H_3Me_2 \cdot COPr^a$ , is a colourless, mobile oil, boils at  $135^{\circ}$  under 17 mm. pressure, and has a sp. gr. 0.9691 at  $21.5^{\circ}/4^{\circ}$ .

1:3-Dimethyl-4- $\alpha$ -hydroxybutylbenzene,  $C_6H_3Me_2 \cdot CHPr^a \cdot OH$ , is a colourless, mobile oil, boils at  $134^{\circ}$  under 14 mm. pressure, and has a sp. gr. 0.9611 at  $13^{\circ}/4^{\circ}$ . The *chloride*,  $C_6H_3Me_2 \cdot CHPr^aCl$ , boils at  $129^{\circ}$  under 14 mm. pressure.

p-Butenyl-m-xylene,  $C_6H_3Me_2 \cdot CH \cdot CHEt$ , is a colourless, mobile liquid, boils at  $114^{\circ}$  under 21 mm. pressure, has a sp. gr. 0.8937 at  $19^{\circ}/4^{\circ}$ , and has an odour suggestive of almonds. The *nitrosochloride*,  $C_{12}H_{16}ONCl$ , separates in white needles and melts at  $135^{\circ}$ .

Butyrylmesitylene,  $C_6H_2Me_3 \cdot COPr^a$ , is a pale yellowish oil, boils at  $140^{\circ}$  under 14 mm. pressure, and yields mesitylene when heated with hydriodic acid.

1:3:5-Trimethyl-2- $\alpha$ -hydroxybutylbenzene,  $C_6H_2Me_3 \cdot CHPr^a \cdot OH$ , is a colourless, somewhat viscous oil, boils at  $147.5^{\circ}$  under 12 mm. pressure, and has a sp. gr. 0.964 at  $17^{\circ}/4^{\circ}$ , and when heated with hydriodic acid it yields, not mesitylene, but *n*-butylmesitylene. The *phenylurethane*,  $C_{20}H_{25}O_2N$ , is prepared with difficulty, and was separated from large quantities of diphenylcarbamide by extracting with benzene; it crystallises from alcohol in white needles and melts at  $119-120^{\circ}$ . The *acetate*,  $C_{15}H_{22}O_2$ , is a colourless liquid, boils at  $140-141^{\circ}$  under 9 mm. pressure, and has a sp. gr. 0.976 at  $14.5^{\circ}/4^{\circ}$ . Butenylmesitylene,  $C_6H_2Me_3 \cdot CH \cdot CHEt$ , is a colourless, mobile oil, boils at  $118-119^{\circ}$  under 14 mm. pressure, and has a sp. gr. 0.8953 at  $14^{\circ}/4^{\circ}$ . The *nitrosochloride*,  $C_{13}H_{18}ONCl$ , separates in colourless crystals and melts at  $122-122.5^{\circ}$ .

m-Xylyl pentadecyl ketone,  $C_6H_3Me_2 \cdot CO \cdot C_{15}H_{31}$ , from palmityl chloride and m-xylene, boils at  $259^{\circ}$  under 11 mm. pressure, and melts at  $35^{\circ}$ .

1:3-Dimethyl-4- $\alpha$ -hydroxyhexadecylbenzene,  $C_6H_3Me_2 \cdot CH(OH) \cdot C_{15}H_{31}$ , crystallises in white, fatty flakes, melts at  $23-24^{\circ}$ , and boils at  $267^{\circ}$  under 20 mm. pressure. Hexadecenyl-m-xylene,  $C_6H_3Me_2 \cdot CH \cdot CH \cdot C_{14}H_{29}$ , is a colourless, viscous oil, boils at  $254^{\circ}$  under 17 mm. pressure, and has a sp. gr. 0.868 at  $20^{\circ}/4^{\circ}$ .

Mesityl pentadecyl ketone,  $C_6H_2Me_3 \cdot CO \cdot C_{15}H_{31}$ , separates from alcohol in crystalline aggregates or glistening flakes with a fatty feeling, boils at  $262^{\circ}$  under 13 mm. pressure, and melts at  $41^{\circ}$ . 1:3:5-Trimethyl-2- $\alpha$ -hydroxyhexadecylbenzene,  $C_6H_2Me_3 \cdot CH(OH) \cdot C_{15}H_{31}$ , crystallises from alcohol in needles, boils at  $274^{\circ}$  under 16 mm. pressure, and melts at  $47.5^{\circ}$ . The *chloride* is a thick, yellowish oil.

Hexadecenylmesitylene,  $C_6H_2Me_3 \cdot CH \cdot CH \cdot C_{14}H_{29}$ , forms long needles, melts at  $28.5-29^{\circ}$ , boils at  $260^{\circ}$  under 23 mm. pressure, and has no appreciable tendency to polymerise.

T. M. L.

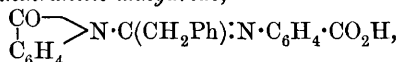
**Separation of Phenylalanine from Amino-acids.** By ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1902, **35**, 210-226).—The authors find that the isolation of phenylalanine by means of its copper derivative as suggested by Schulze and Barbieri

(Abstr., 1883, 1122), is accompanied with loss of material in the presence of aminovaleric acid and fails entirely in the presence of a large proportion of leucine such as occurs in the hydrolytic products of conglutin.

Mercuric nitrate is found to precipitate phenylalanine incompletely in presence of leucine and a better separation is secured by the subsequent addition of sodium carbonate. Phosphotungstic acid precipitates phenylalanine from solutions containing 0.25 per cent. of this substance alone, and from more concentrated solutions even in presence of other amino-acids, the separation in both cases being improved by the addition of a small quantity of sulphuric acid. With the aid of this reagent, phenylalanine has been isolated from etiolated seedlings of *Lupinus albus* and *Vicia sativa*, and from the products of alkaline hydrolysis of conglutin and of the proteid of pumpkin seeds. This method of isolation does not interfere with the eventual separation of other amino-acids which may be present. The phosphotungstic compound is soluble in boiling water, slightly so in cold (72 per cent. at 15—16°), and readily in alcohol; it crystallises from hot water in silky leaflets, from which the amino-acid is regenerated in a pure state by addition of excess of baryta water, the latter being in turn removed by carbon dioxide.

T. A. H.

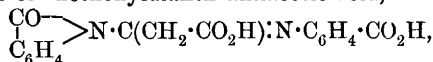
**Amidine Derivatives of Anthranilic Anhydride.** By STEFAN VON NIEMENTOWSKI (*Bull. Acad. Sci. Cracow*, 1902, 232—234).—*Phenylethylenyldianthranilic anhydride*,



formed by boiling anthranilic acid with phenylacetic acid or its ethylester for several days, crystallises in long, greenish-yellow leaflets, is soluble with difficulty in benzene or alcohol, more easily in acetone or ethyl acetate, and melts at 283°. The *platinichloride*,  $(\text{C}_{22}\text{H}_{16}\text{O}_3\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6$ , melts and decomposes at 256—258°. Prolonged boiling in alkaline solution results in the formation of *phenylethylenyldianthranilic acid*, which crystallises in small, colourless prisms and melts and effervesces at 190°. The silver salt,  $\text{C}_{22}\text{H}_{16}\text{O}_4\text{N}_2\text{Ag}_2$ , forms a white precipitate, very sensitive to light.

When the anhydride is heated with concentrated hydrochloric acid at 210°, it loses 1 mol. of carbon dioxide and forms *phenylethylenylanilanthranilic anhydride*,  $\begin{array}{c} \text{CO} \\ | \\ \text{C}_6\text{H}_4 \end{array} \text{>N} \cdot \text{C}(\text{CH}_2\text{Ph}) \cdot \text{NPh}$ , which crystallises in white, silky needles and melts at 229°.

The *anhydride* of methenyldianthranilacetic acid,



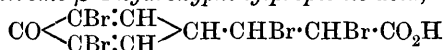
obtained by heating 2 mols. of anthranilic acid with 1 mol. of ethyl malonate, is insoluble or only slightly soluble in all solvents, crystallises in microscopic plates, melts and decomposes at 302°, and, when heated in alkaline solution, is hydrolysed to *methenyldianthranilacetic acid*, which is easily soluble in organic solvents or hot water, crystallises in thin, small prisms, and melts and effervesces at 190°. *Malon-*



*tetranthranilic dianhydride*,  $\text{CH}_2\left[\text{C}(\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})\cdot\text{N}\begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix}\right]_2$ , obtained by heating 4 mols. of anthranilic acid with 1 mol. of ethyl malonate, is soluble with difficulty in acetic acid, easily in phenylhydrazine, crystallises in yellow needles, melts and effervesces at  $275^\circ$ , and is hydrolysed by boiling aqueous alkalis to *malontetranilic acid*, which crystallises in white needles, is soluble with difficulty in organic solvents, easily soluble in alkalis, insoluble in dilute acids, and melts and decomposes at  $263\text{--}265^\circ$ . G. Y.

**Action of Bromine on *p*-Hydroxycinnamic Acid; Tetrabromo-*p*-hydroxycinnamic Acid.** Brominated *p*-Vinyl- and *p*-Ethyl-phenol Derivatives. By THEODOR ZINCKE and FR. LEISSE (*Annalen*, 1902, 322, 220—238. Compare this vol., i, 605).—*p*-Hydroxycinnamic acid yields a *methyl* ester crystallising in white needles melting at  $137^\circ$ .

$\alpha\beta\text{-}3:5$ -Tetrabromo- $\beta$ -4-hydroxyphenylpropionic acid,



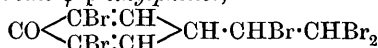
or  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$ , obtained by heating *p*-hydroxycinnamic acid with bromine on the water-bath, crystallises from glacial acetic acid in white needles melting at  $191^\circ$ ; when treated with hydriodic acid, it yields 3:5-dibromo- $\beta$ -4-hydroxyphenylpropionic acid melting at  $114^\circ$ , and not at  $107\text{--}108^\circ$  (compare Stöhr, *Abstr.*, 1884, 1349); the *methyl* ester of this product crystallises in white needles melting at  $55^\circ$ .

*Methyl*  $\alpha\text{-}3:5$ -tribromo- $\beta$ -methoxy- $\beta$ -4-hydroxyphenylpropionate,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}(\text{OMe})\cdot\text{CHBr}\cdot\text{CO}_2\text{Me}$ , produced by heating the tetrabromo-acid with alcohol and hydrogen chloride, crystallises from this solvent in white needles melting at  $142^\circ$ ; its *acetyl* derivative forms short, white needles and melts at  $142^\circ$ .

$\alpha\text{-}3:5$ -Tribromo- $\beta$ -methoxy- $\beta$ -4-hydroxyphenylpropionic acid,  $\text{OH}\cdot\text{CH}_2\text{Br}_2\cdot\text{CH}(\text{OEt})\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$ , obtained by boiling the tetrabromo-acid with ethyl alcohol, crystallises in lustrous white needles and melts at  $174^\circ$ ; its methyl ester is oily, but yields an *acetyl* derivative crystallising in white leaflets and melting at  $119^\circ$ .

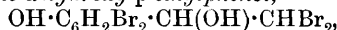
$\beta\text{-}3:5$ -Tribromo-*p*-vinylphenol,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}\cdot\text{CHBr}$ , produced by the action of alcoholic potassium hydroxide on the tetrabromo-acid, crystallises in lustrous, white needles and melts at  $110^\circ$ ; the *acetyl* derivative forms white needles melting at  $124^\circ$ .

$\alpha\beta\text{-}3:5$ -Pentabromo- $\psi$ -*p*-ethylphenol,



or  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CHBr}\cdot\text{CHBr}_2$ , is readily prepared by adding bromine to the preceding compound, and was once obtained by the direct action of the halogen on *p*-ethylphenol; it crystallises in needles or prisms and melts at  $106\text{--}107^\circ$ .

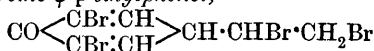
$\beta\text{-}3:5$ -Tetrabromo- $\alpha$ -hydroxy-*p*-ethylphenol,



produced by warming the preceding compound with dilute acetone, crystallises from a mixture of benzene and petroleum in needles melting at

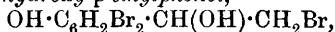
147—148°; its diacetyl compound forms colourless prisms and melts at 103°. The *methoxy*-derivative,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}(\text{OMe})\cdot\text{CHBr}_2$ , prepared by the action of methyl alcohol, separates in colourless needles and melts at 72°.

$\alpha\beta$ -3 : 5-Tetrabromo- $\psi$ -*p*-ethylphenol,



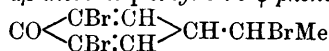
or  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$ , is readily prepared by adding hydrogen bromide to the preceding vinyl compound, and was also once obtained from *p*-ethylphenol; it crystallises from light petroleum in colourless needles melting at 123°. This substance is readily converted by reduction into 3 : 5-dibromo-*p*-vinylphenol, a compound crystallising in leaflets and melting at 73—74°.

$\beta$ -3 : 5-Tribromo- $\alpha$ -hydroxy-*p*-ethylphenol,



produced by the action of dilute acetone on the preceding tetrabromo-compound, separates in monoclinic prisms and melts at 107°; its diacetyl derivative melts at 103°. The corresponding *methyl* compound,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}(\text{OMe})\cdot\text{CH}_2\text{Br}$ , crystallises in needles melting at 112°, and the *ethyl* derivative forms white plates melting at 86°.

3 : 5-Dibromo-*p*-vinylphenol yields an *acetyl* derivative crystallising in white leaflets and melting at 76—77°; it also gives rise to an oily tribromo-derivative,  $\alpha\beta$ -dibromo-*p*-ethyl-3 : 5- $\psi$ -phenol,



or  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CHMeBr}$ , on treatment with hydrogen bromide; this product, when warmed with dilute acetic acid, furnishes 3 : 5-dibromo- $\alpha$ -hydroxy-*p*-ethylphenol,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CHMe}\cdot\text{OH}$ , which crystallises in rectangular plates and melts at 149°; its *diacetyl* derivative separates in needles melting at 55—56°. The  $\alpha$ -*methyl* derivative crystallises in hard needles and melts at 100—101°, whilst the  $\alpha$ -*ethyl* compound forms thick, prismatic crystals and melts at 99—100°. G. T. M.

**Colouring Matters obtainable by the Action of Isatin on Extracts of Isatis Tinctoria.** By LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1902, 227—230).—Results identical with Beyerinck's (*Abstr.*, 1900, i, 230, 649) are obtained by treating the fresh leaves of *Isatis tinctoria* with boiling water, but on extracting the dried leaves with alcohol a substance is obtained which, on treatment with isatin in aqueous solution, yields a colouring matter, *isatocyanin*, a blackish-brown powder which dissolves easily in glacial acetic acid and sparingly in alcohol to blue solutions which become colourless on keeping; it dissolves in boiling phenol and is reprecipitated by ether; in concentrated sulphuric acid, it forms a yellow solution which becomes blue on keeping. The absorption spectrum shows a band with maximum intensity at the sodium line. Isatocyanin resembles but is not identical with the colouring matters obtained by the action of pyrrolidine on isatin, and of acetic anhydride on the condensation product of piperidine and isatin. The spectrum of the former shows general absorption of the red, of the latter, a band with maximum intensity at  $\lambda$  618—661. G. Y.

**Synthesis of  $\alpha$ -Truxillic Acid.** By C. N. RIIBER (*Ber.*, 1902, 35, 2411—2415).—Molecular weight determinations from the boiling point of solutions in acetone have shown that Liebermann's white cinnamylidene-malonic acid (Abstr., 1895, i, 470) is a bimolecular compound. When oxidised with alkaline permanganate, it yields Liebermann's  $\alpha$ -truxillic acid (Abstr., 1889 1194; 1890, 1424) identical with that found with the cocaine alkaloids; the bimolecular acid has therefore the constitution  $C(CO_2H)_2 \cdot CH \cdot CH < \begin{smallmatrix} CHPh \\ CHPh \end{smallmatrix} > CH \cdot C(CO_2H)_2$ .

When distilled in an absolute vacuum, it loses carbon dioxide and leaves an *acid*,  $C_{22}H_{20}O_3$ , isomeric with the two known cinnamylidene-acetic acids; this separates from dilute alcohol in microscopic needles and melts at  $204^\circ$ .  $\alpha$ -Truxillic acid sublimes unchanged in an absolute vacuum. T. M. L.

#### Esterification of Unsymmetrical Di- and Poly-basic Acids.

**IV. Conductivity of some Acids and Acid Esters.** By RUDOLF WEGSCHEIDER (*Monatsh.*, 1902, 23, 317—356. Compare Abstr., 1901, i, 32).—3-Nitrophthalic acid commences to show dibasic dissociation at the dilution  $v=514$ , and has a conductivity  $K$  1.31 (compare Ostwald, Abstr., 1889, 818). A specimen of the  $\alpha$ -monomethyl ester, previously found to melt at  $142^\circ$ , now melts at  $146$ — $149^\circ$ . It is probable that this ester occurs in two forms, the labile form melting at  $144^\circ$ , the stable form at  $152$ — $153^\circ$  (compare McKenzie, Trans., 1901, 79, 1141). The  $\beta$ -monomethyl ester [ $CO_2Me : CO_2H : NO_2 = 1 : 2 : 3$ ] is now found to have the conductivity  $K$  1.6

4-Nitrophthalic acid commences to show dibasic dissociation at the dilution  $v=256$ , but does not do so strongly until  $v=1024$ . The author considers his value,  $K$  0.77, as probably more correct than Ostwald's (*loc. cit.*). The monomethyl ester has a conductivity  $K$  0.46. 4-Hydroxyphthalic acid does not show dibasic dissociation at the dilution  $v=1033$ ; it has a conductivity  $K$  0.12. Only one *monomethyl ester* could be obtained; it melts at  $166^\circ$ , and has a conductivity  $K$  0.0205. The *dimethyl ester* has a conductivity  $K$   $10^{-5}$  (?), resembling *para*- and *meta*-nitrophenol.

3:6-Dichlorophthalic acid commences to show dibasic dissociation at a slightly greater dilution than  $v=51$ , it has a conductivity  $K$  3.45. The monomethyl ester is easily hydrolysed by warm water; it has a conductivity  $K$  1.5. Kirpal's conductivity constant,  $K$  0.11, for hemipinic acid (Abstr., 1898, i, 87) is confirmed. That the value of  $K$  for hemipinic acid is lower than for *m*-hemipinic acid, shows that the multiplication of substituting groups leads occasionally to abnormal results. *n*-Propylhydrogen hemipinate has a conductivity  $K$  0.0144, the  $\beta$ -acid ester has  $K$  0.093. Bromoterephthalic acid shows dibasic dissociation at dilutions over  $v=255$ ; it has a conductivity  $K$  0.62. The  $\alpha$ -monomethyl ester has most probably the constitution [ $CO_2H : Br : CO_2Me = 1 : 3 : 4$ ], and the corresponding  $\beta$ -ester (m. p.  $164^\circ$ ) [ $CO_2H : Br : CO_2Me = 1 : 2 : 4$ ] (compare Abstr., 1900, i, 658).

Nitroterephthalic acid shows dibasic dissociation at dilutions greater than  $v=32$ ; it has a conductivity  $K$  1.87. The  $\alpha$ -monomethyl ester

[ $\text{CO}_2\text{H}:\text{NO}_2:\text{CO}_2\text{Me}=1:3:4$ ], melts at  $174-175.5^\circ$ , and has a conductivity  $K\ 0.0770$ . The  $\beta$ -monomethyl ester [ $\text{CO}_2\text{H}:\text{NO}_2:\text{CO}_2\text{Me}=1:2:4$ ] melts at  $133-134^\circ$ , and has a conductivity  $K\ 1.90$ .

Hydroxyterephthalic acid shows dibasic dissociation at the dilution  $v=200$ ; it has a conductivity  $K\ 0.269$ . The  $\alpha$ -monomethyl ester has a conductivity  $K\ 0.025$ ; the  $\beta$ -ester resembles salicylic acid in its ferric chloride reaction and its solubility in chloroform, it has a conductivity  $K\ 0.277$ .

The  $\beta$ -monomethyl ester of papaveric acid is easily hydrolysed by water; the most accurate conductivity constant,  $K\ 0.39$ , is probably correct to  $\pm 20$  per cent., the same accuracy is obtained for the conductivity  $K\ 0.61$  of the  $\gamma$ -monomethyl ester. These results agree with the formulæ proposed by Goldschmiedt and Kirpal for these methyl esters (Abstr., 1897, i, 131).

*m*-Sulphobenzoic acid follows Ostwald's law of dilution to  $v=90$ ; at  $v=180$  it shows dibasic dissociation, and has the conductivity  $K\ 40$  (?), van't Hoff's dissociation constant  $k$  rises from  $k\ 1.69$  at  $v=11.27$  to  $k\ 4.66$  at  $v=90.6$ . It is shown by calculations from the conductivity of benzenesulphonic acid that the behaviour of  $k$  depends on the value chosen for  $\mu_\infty$ . With  $\mu_\infty=360$ ,  $k$  rises from  $1.61$  at  $v=32$  to  $7.77$  at  $v=1024$ , whereas with  $\mu_\infty=366$ ,  $k$  remains approximately constant.

It would seem as if variations from Ostwald's law of dilution depend on the nature as well as on the concentration of the ions.  $\alpha$ -Methyl hydrogen *m*-sulphobenzoate [ $\text{CO}_2\text{H}:\text{SO}_3\text{Me}$ ] melts at  $138^\circ$ , is easily hydrolysed by water, and has a conductivity  $K\ 0.068$ . The  $\beta$ -monomethyl ester [ $\text{CO}_2\text{Me}:\text{SO}_3\text{H}$ ], is very soluble in water and has a conductivity  $K\ 20$  (?). Tribromobenzoic acid has a conductivity  $K\ 3.90$ .

Applying the formula  $K_\alpha + K_\beta = aK$  (Abstr., 1895, ii, 310) to the present results, greater variations are found in the factor  $a$  (mean value  $a=0.90$ ). It is apparent that the stronger the dibasic acid the smaller the dilution at which dibasic dissociation becomes marked.

G. Y.

### Esterification of Unsymmetrical Di- and Poly-basic Acids.

V. Constitution of some Acid Esters. By RUDOLF WEGSCHIEDER (*Monatsh.*, 1902, 23, 357—368. Compare foregoing abstract).—The conductivity of methyl hydrogen 4-hydroxyphthalate agrees with that calculated for the  $\alpha$ -acid ester [ $\text{CO}_2\text{H}:\text{CO}_2\text{Me}:\text{OH}=1:2:4$ ]. The calculated conductivities of the  $\alpha$ - and  $\beta$ -monomethyl esters of 4-nitrophthalic acid are too close to admit of any conclusion as to the constitution of the acid ester formed.

The conductivities of the *ortho*- and *allo*-methyl hydrogen camphorates agree with different formulæ proposed by Bouveault, Bredt, Perkin, and Schryver, but not with those proposed by Tiemann and Wagner.

The conductivities of  $\alpha$ - and  $\beta$ -monomethyl esters of tricarballic acid (Bone and Sprankling, *Trans.*, 1902, 81, 34) do not agree with those calculated. The affinity constant of the monomethyl ester of *aa*-dimethyltricarballic acid, obtained by hydrolysis of the trimethyl

ester, agrees with the formula  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}(\text{CO}_2\text{Me})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ . The ester obtained by direct esterification agrees in its conductivity with the formula  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ . G. Y.

**Esterification of Unsymmetrical Di- and Poly-basic Acids.**  
 VI. By RUDOLF WEGSCHEIDER (*Monatsh.*, 1902, 23, 369—392).—Methyl opianate (m. p.  $81-84^\circ$ ) gives with *m*-phenylenediamine hydrochloride in aqueous or alcoholic solution a light yellow colour which becomes darker on standing (*Abstr.*, 1897, ii, 468), giving evidence of the presence of an aldehyde group.  $\psi$ -Methyl opianate gives no reaction.

Treatment of  $\psi$ -methyl opianate in absolute ethereal solution with hydrogen peroxide, chromium trioxide, or chloranil does not lead to formation of  $\beta$ -monomethyl hemipinate, except perhaps in traces. Treatment of the  $\psi$ -methyl ester with potassium permanganate in acetone solutions leads to the formation of opianic anhydride and a substance,  $\text{C}_{23}\text{H}_{29}\text{O}_{11}$ , which crystallises in large, clear, colourless prisms and melts at  $192-194^\circ$ .

$\beta$ -Ethyl hydrogen hemipinate is only slightly hydrolysed by cold aqueous or alcoholic ammonia; on heating with alcoholic ammonia at  $125^\circ$ , a trace of hemipinimide is formed.

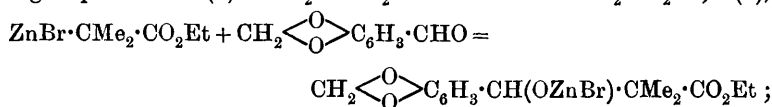
$\alpha$ -Methyl hydrogen hydroxyterephthalate is formed by boiling the potassium hydrogen salt with methyl sulphate in methyl alcohol solution; excess of methyl sulphate leads to the formation of the dimethyl ester. By heating the potassium acid salt with methyl iodide and methyl alcohol at  $100^\circ$ , the  $\beta$ -monomethyl ester is formed (compare *Abstr.*, 1900, i, 658). When hydrolysed by 1 mol. of potassium hydroxide in methyl alcohol solution, dimethyl papaverate yields a mixture of the  $\beta$ - and  $\gamma$ -monomethyl esters, along with a small quantity of free acid. The  $\gamma$ -ester is sparingly soluble in cold methyl alcohol, from which it easily crystallises; the  $\beta$ -ester is easily soluble. When acted on by methyl alcohol, papaveric anhydride forms principally the  $\beta$ -monomethyl ester (m. p.  $156-157^\circ$ ), and a small quantity of the  $\gamma$ -monomethyl ester. G. Y.

**Esterification of Unsymmetrical Di- and Poly-basic Acids.**  
 VII. Esterification of 4-Hydroxyphthalic Acid. By RUDOLF WEGSCHEIDER and RICHARD PIESEN (*Monatsh.*, 1902, 23, 393—404).— $\alpha$ -Methyl hydrogen 4-hydroxyphthalate (m. p.  $166^\circ$ ) is formed by the action of methyl alcohol on the acid, with or without addition of mineral acids, by partial hydrolysis of the dimethyl ester by potassium hydroxide, by the action of methyl alcohol on the anhydride, and by the action of methyl iodide on the acid potassium salt. The isomeric ester was not obtained by the action of sodium methoxide on the anhydride. The  $\alpha$ -monomethyl ester crystallises from water in broad needles and gives a yellow coloration with ferric chloride in aqueous solution. The dimethyl ester is easily formed by the action of methyl alcohol on the acid in presence of hydrogen chloride or sulphuric acid; it dissolves in benzene, is reprecipitated by addition of light petroleum, and melts at  $104^\circ$ . One mol. of the dimethyl ester requires 0.65 mol. of potassium hydroxide for neutralisation; 1 mol. of monomethyl ester

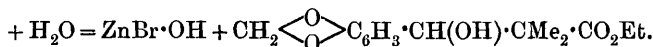
requires 1.16 mols. of potassium hydroxide, and 1 mol. of the acid requires 1.94 mols. of potassium hydroxide, the acidity of the phenolic hydroxyl increasing with esterification of the carboxylic groups. 4-Hydroxyphthalic anhydride is best prepared by heating the acid at 200° in a stream of hydrogen or carbon dioxide. G. Y.

**Esterification of Unsymmetrical Di- and Poly-basic Acids.**  
**VIII. Esterification of Nitroterephthalic Acid. II.** By RUDOLF WEGSCHEIDER [and, in part, by RICHARD PIESEN and OTTO BREYER] (*Monatsh.*, 1902, 23, 405—414. Compare Abstr., 1900, i, 657).—On partial hydrolysis by potassium hydroxide or hydrochloric acid, dimethylnitroterephthalate yields  $\alpha$ -methyl hydrogen nitroterephthalate along with a small quantity of the  $\beta$ -monomethyl ester. The  $\alpha$ -acid ester is also formed by the action of methyl iodide on potassium hydrogen nitroterephthalate. It crystallises from water or benzene in microscopic, thick prisms. The  $\beta$ -acid ester is formed by the action of methyl alcohol on the acid in the presence of mineral acids along with the dimethyl ester. It crystallises from benzene in needles which melt at 133—134°, from water in crystals containing 1H<sub>2</sub>O and melting at 80°. G. Y.

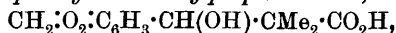
**Action of Zinc and Ethyl Bromoisobutyrate on Piperonaldehyde.** Synthesis of  $\alpha$ -Dimethyl- $\beta$ -hydroxy- $\beta$ -piperonylpropionic Acid. By P. MUSCHINSKY (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 370—375).—Reformatsky's method of preparing tertiary hydroxyacids by the action of a mixture of zinc and a monohaloid ester on a compound containing a carbonyl group, is found to fail when the last-named compound is an aromatic aldehyde containing a hydroxyl group in the benzene nucleus. In order to decide whether the cause of such failure lies in the presence of the hydroxyl group or of non-carbonyl oxygen in general, the author has studied the action of zinc and ethyl bromoisobutyrate on piperonaldehyde, the result indicating that it is the hydroxyl group which prevents the reaction in the above-mentioned cases. The reaction here considered proceeds according to the following equations: (1)  $\text{CMe}_2\text{Br}\cdot\text{CO}_2\text{Et} + \text{Zn} = \text{ZnBr}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ ; (2),



and (3), this last

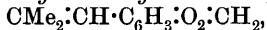


*$\beta$ -Hydroxy- $\beta$ -piperonyl- $\alpha$ -dimethylpropionic acid,*



separates from water in slender crystals which melt and decompose at 156°; it is readily soluble in alcohol or ether and has the normal molecular weight in boiling ether. The *sodium* (with 4H<sub>2</sub>O), *barium* (with 6H<sub>2</sub>O), and *silver* salts were prepared and analysed. When heated

with dilute sulphuric acid, the acid gives up carbon dioxide and water, forming 2:3-methylenedioxy-1-isobutylenebenzene,

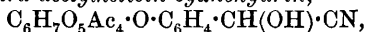


which boils at 252—254° and has the sp. gr. 1.094 at 22°/22°.

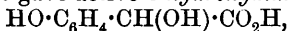
T. H. P.

**Asymmetric Synthesis.** By EMIL FISCHER and MAX SLIMMER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 597—610).—*Tetra-acetylhelicin*, obtained by the action of acetic anhydride on helicin in presence of sodium acetate, melts at 142° (corr.). In solution in benzene, it has  $[\alpha]_D - 23.48^\circ$  at 20°; whilst in solution in acetone it has  $[\alpha]_D - 37.15^\circ$  at 20°.

When treated with anhydrous hydrogen cyanide, it liquefies at first, then crystals of *tetra-acetylhelicin cyanohydrin*,



separate. This compound is easily soluble in chloroform, acetone, or hot alcohol, sparingly in ether or benzene, and almost insoluble in water; it melts at 162° (corr.) and has  $[\alpha]_D - 24.32^\circ$  at 20°. The conversion of the cyanohydrin into *tetra-acetylgluco-o-hydroxymandelamide* can be effected by the action of hydrogen chloride, but special precautions are necessary; it melts at 205° (corr.). Saponification of the amide to *gluco-o-hydroxymandelic acid* was not possible, but when warmed with dilute mineral acids, it gave active *o-hydroxymandelic acid*,



which has  $[\alpha]_D + 1.9^\circ$  at 20°. Preparation of this active *o-hydroxymandelic acid* without isolation of the amide led to a product with  $[\alpha]_D + 1.3^\circ$  at 20°.

This is pointed out as a case where, by synthesis, an active asymmetric compound is produced. On account of the small rotatory power of the product and the consequent indefiniteness of the proof of this important synthesis, another reaction has been tried to bring about the desired end, namely, by producing a carbinol through the intervention of zinc alkyl.

When *tetra-acetylhelicin* is treated in benzene solution with zinc ethyl and the resulting product decomposed with water, *tetra-acetylgluco-o-hydroxyphenylethylcarbinol*,  $\text{C}_6\text{H}_7\text{O}_5\text{Ac}_4\cdot\text{O}\cdot\text{CHEt}\cdot\text{OH}$ , is obtained which crystallises in square plates melting at 156.5° (corr.), and having  $[\alpha]_D - 30.10^\circ$  at 20°. When saponified in the cold with baryta water, it gives *gluco-o-hydroxyphenylethylcarbinol*, but this was not obtained in a satisfactory form. Without isolating this glucoside, the *tetra-acetylcarbinol* can be converted into active *o-hydroxyphenylethylcarbinol*,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CHEt}\cdot\text{OH}$ , by treating the mixture after saponification with baryta with sulphuric acid and extracting with ether. By distilling under a pressure of 0.3 mm., a thick, colourless oil was obtained which in acetone solution has  $[\alpha]_D - 9.83^\circ$  at 20°. An active substance has, therefore, undoubtedly been produced by synthesis.

For the sake of comparison, inactive *o-hydroxyphenylethylcarbinol* has been prepared and incidentally the following compounds:—*Methylsalicylic chloride* was obtained as a colourless liquid boiling at 145° under 17 mm. pressure, by the action of thionyl chloride on methylsalicylic acid. This acid chloride in ethereal solution, when

treated with zinc ethyl and the product decomposed with water, gives *o*-methoxyphenyl ethyl ketone,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{COEt}$ , as a slightly yellow, sweet-smelling liquid which boils at  $137^\circ$  (corr.) under 16.5 mm. pressure. This methoxy-compound when heated at  $110^\circ$  in a sealed tube with concentrated hydrochloric acid gives *o*-hydroxyphenyl ethyl ketone,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{COEt}$ , which boils at  $115^\circ$  (corr.) under 15 mm. pressure, and resembles phenol in odour. Its sodium salt is sparingly soluble in concentrated alkali solution and crystallises easily from alcohol.

By reducing an alkaline solution of the ketone with sodium amalgam and extraction with ether, *i*-*o*-hydroxyphenylethylcarbinol is obtained; this boils at about  $125\text{--}130^\circ$  under 0.25 mm. pressure, is only slightly soluble in hot water, and is little volatile with steam. It is very easily resinified by mineral acids, and reduces Fehling's solution when heated. In all these properties it closely resembles the active compound described above. J. McC.

**Disulphones. XI. Influence of Intranuclear Substituents on the Reactivity of Aromatic Aldehydes and Ketones.** By THEODOR POSNER (*Ber.*, 1902, 35, 2343—2354. Compare Abstr., 1899, i, 604; 1900, i, 5, 16; 1901, i, 14, 88, 474, 703; this vol., i, 82, 220, 296).—Benzophenone and acetophenone interact only with the more reactive mercaptans, but do not condense with amyl or phenyl mercaptan.

*Dithiobenzylidiphenylmethane (benzophenonebenzylmercaptal),*  
 $\text{CPh}_2(\text{S}\cdot\text{CH}_2\text{Ph})_2$ ,

produced by condensing benzophenone and benzyl mercaptan with hydrogen chloride dissolved in glacial acetic acid, crystallises from water in white needles melting at  $144^\circ$ .

*Dibenzylsulphodiphenylmethane (benzophenonedibenzylsulphone),*  
 $\text{CPh}_2(\text{SO}_2\cdot\text{CHPh})_2$ ,

results from the oxidation of the preceding substance dissolved in carbon tetrachloride with cold saturated potassium permanganate solution; it separates from alcohol as a white, crystalline powder melting at  $204\text{--}208^\circ$ . Acetophenone and benzyl mercaptan condense to yield an unstable, oily mercaptal, which, on oxidation, gives rise to *aa*-*dibenzylsulpho-a-phenylethane (acetophenonedibenzylsulphone),*

$\text{CMePh}(\text{SO}_2\cdot\text{CH}_2\text{Ph})_2$ ,

a compound crystallising from alcohol in pale yellow leaflets melting at  $131\text{--}133^\circ$ . The presence of a nitro-group in the ortho-position with respect to the carbonyl radicle greatly diminishes the reactivity of the aromatic aldehydes, and quite prevents the condensation of the corresponding ketones with the thioalcohols. On the other hand, the introduction of nitro-groups into the meta- or para-position actually increases the capacity for reaction, and *m*-nitroacetophenone interacts with the less reactive mercaptans, whereas these substance do not condense with acetophenone itself.

The oily mercaptal obtained from *o*-nitrobenzaldehyde and ethyl mercaptan yields, on oxidation, *diethylsulpho-o-nitrophenylmethane (o-nitrobenzaldehydediethylsulphone),*  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{SO}_2\text{Et})_2$ , crystallising from alcohol in lustrous, colourless needles melting at  $138^\circ$ .

*Dibenzylsulpho-o-nitrophenylmethane (o-nitrobenzaldehydedibenzylsul-*

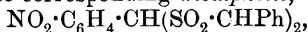


phone),  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{SO}_2\text{CH}_2\text{Ph})_2$ , obtained in a similar manner, crystallises in white leaflets melting at  $188-190^\circ$ .

*Diphenylsulpho-o-nitrophenylmethane* (o-nitrobenzaldehydediphenylsulphone),  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{SO}_2\text{Ph})_2$ , produced by oxidising the condensation product of o-nitrobenzaldehyde and thiophenol, crystallises in thin flakes melting at  $158-160^\circ$ .

*Diethylsulpho-m-nitrophenylmethane* (m-nitrobenzaldehydediethylsulphone), separates in white, flocculent crystals and melts at  $164^\circ$ .

*Dithiobenzyl-m-nitrophenylmethane* (m-nitrobenzaldehydebenzylmercaptan),  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{S} \cdot \text{CH}_2\text{Ph})_2$ , forms colourless, granular crystals and melts at  $56^\circ$ ; the corresponding disulphone,

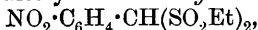


is a white, crystalline powder melting at  $194^\circ$ .

*Diamylsulpho-m-nitrophenylmethane* (m-nitrobenzaldehydediamylsulphone),  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{SO}_2 \cdot \text{C}_5\text{H}_{11})_2$ , crystallises from hot alcohol in white leaflets and melts at  $120-122^\circ$ ; the corresponding diphenyldisulphone,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{SO}_2\text{Ph})_2$ , melts at  $176^\circ$ .

*Dithiobenzyl-p-nitrophenylmethane* (p-nitrobenzaldehydebenzylmercaptan),  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{S} \cdot \text{CH}_2\text{Ph})_2$ , crystallises from alcohol in colourless needles or leaflets, melts at  $72-74^\circ$ , and yields a disulphone separating from glacial acetic acid as a yellow, crystalline powder melting at  $244^\circ$ .

p-Nitrobenzaldehyde also yields a diethyldisulphone,



a white, crystalline powder melting at  $172^\circ$ ; a diamyldisulphone,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{SO}_2 \cdot \text{C}_5\text{H}_{11})_2$ , crystallising in white leaflets and melting at  $108-110^\circ$ ; a diphenyldisulphone forming colourless needles and melting at  $210-212^\circ$ .

*aa-Diethylsulpho-m-nitro-a-phenylethane* (m-nitroacetophenonediethylsulphone),  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CMe}(\text{SO}_2\text{Et})_2$ , derived from m-nitroacetophenone and ethyl mercaptan, forms lustrous, white needles melting at  $140-142^\circ$ .

*aa-Dithiobenzyl-m-nitro-a-phenylethane* (m-nitroacetophenonebenzylmercaptan),  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CMe}(\text{S} \cdot \text{CH}_2\text{Ph})_2$ , is obtained in granular crystals melting at  $82-84^\circ$ ; the corresponding disulphone is a crystalline powder melting at  $128-130^\circ$ .

*aa-Diamylsulpho-m-nitro-a-phenylethane* (m-nitroacetophenonediamylsulphone),  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CMe}(\text{SO}_2 \cdot \text{C}_5\text{H}_{11})_2$ , and the corresponding diphenyldisulphone, crystallise from alcohol in needles melting respectively at  $130-133^\circ$  and  $160-163^\circ$ .

*aa-Diethylsulpho-a-p-nitro-a-phenylethane* (p-nitroacetophenonediethylsulphone),  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CMe}(\text{SO}_2\text{Et})_2$ , is readily obtained from p-nitroacetophenone and ethyl mercaptan; it separates from alcohol in pale yellow leaflets and melts at  $108-110^\circ$ .

*m-Nitrophenyldiethylsulphophenylmethane* (m-nitrobenzophenonediethylsulphone),  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}(\text{SO}_2\text{Et})_2$ , derived from m-nitrobenzophenone and ethyl mercaptan, is a crystalline powder melting at  $175^\circ$ .

*m-Nitrophenyldibenzylsulphophenylmethane* (m-nitrobenzophenonedibenzylsulphone),  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}(\text{SO}_2 \cdot \text{CH}_2\text{Ph})_2$ , is a white powder, crystallising from alcohol and melting at  $184-186^\circ$ .

*p-Nitrophenyldiethylsulphophenylmethane* (p-nitrobenzophenonediethylsulphone),  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}(\text{SO}_2\text{Et})_2$ , crystallises from alcohol as a pale yellow powder and melts at  $193-5^\circ$ .

*p*-Nitrophenyldibenzylsulphophenylmethane (*p*-nitrobenzophenonedibenzylsulphone),  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}(\text{SO}_2 \cdot \text{CH}_2\text{Ph})_2$ , crystallises in colourless needles and melts at  $204^\circ$ .

It was not found possible to condense the mercaptans with aromatic aldehydes or ketones containing hydroxy- or amidogen radicles. Crystalline products were obtained by the oxidation of the *m*- and *p*-amino-derivatives of benzophenone, but these compounds were found to be azo-derivatives containing no sulphur.

*m*-Azobenzophenone,  $\text{N}_2(\text{C}_6\text{H}_4 \cdot \text{COPh})_2$ , crystallises from alcohol in yellowish-brown leaflets and melts at  $141\text{--}142^\circ$ ; *p*-azobenzophenone separates from ethyl acetate in red leaflets having a metallic reflex and melting at  $217^\circ$ .

The disulphones containing nitro-groups in the ortho- or para-position with respect to the carbonyl carbon atom are quite indifferent towards tin and hydrochloric acid and not altered by prolonged heating with this reagent.

The disulphones derived from *m*-nitroacetophenone and the diethyl-disulphones are readily reduced to aminodisulphones, but the yields are small; the disulphones from *m*-nitrobenzaldehyde and *m*-nitrobenzophenone do not usually give rise to definite reduction products.

$\alpha$ -Diethylsulpho-*m*-amino- $\alpha$ -phenylethane (*m*-aminoacetophenonedithylsulphone),  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CMe}(\text{SO}_2\text{Et})_2$ , is a pale yellow, crystalline substance melting at  $136\text{--}138^\circ$ ; it crystallises from alcohol and is readily soluble in dilute hydrochloric acid.

$\alpha$ -Dibenzylsulpho-*m*-amino- $\alpha$ -phenylethane (*m*-aminoacetophenonedibenzylsulphone),  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CMe}(\text{SO}_2 \cdot \text{CH}_2\text{Ph})_2$ , and the corresponding aminodiphenylsulphone,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CMe}(\text{SO}_2\text{Ph})_2$ , are yellow, crystalline powders readily soluble in alcohol or in mineral acids; they melt respectively at  $180\text{--}182^\circ$  and  $158\text{--}160^\circ$ .

*m*-Aminophenyldiethylsulphophenylmethane (*m*-aminobenzophenonedithylsulphone),  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}(\text{SO}_2\text{Et})_2$ , is a white, crystalline powder melting at  $183\text{--}184^\circ$ ; it dissolves in cold dilute hydrochloric acid, and the solution rapidly yields a sparingly soluble hydrochloride, which separates in aggregates of silky needles melting at  $201^\circ$ . G. T. M.

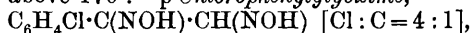
**Compounds of Aromatic Ketones with Orthophosphoric Acid.** By AUGUST KLAGES (*Ber.*, 1902, 35, 2313—2315).—Diortho-substituted aromatic ketones do not form additive compounds with phosphoric acid (compare Klages and Allendorff, *Abstr.*, 1898, i, 477); ketones of the type of acetophenone, however, give, as a rule, salts of the general formula  $\text{COPhR} \cdot \text{H}_3\text{PO}_4$ . Thus acetophenone, *p*-diacetylbenzene, *p*-acetyltoluene, *p*-acetyethylbenzene, acetyl-*o*-xylene, acetyl-*p*-xylene, acetyl-*m*-xylene, diacetyl-*m*-xylene, acetyl- $\psi$ -cumene, acetyl-cumene, acetylanisole, acetylphenetole, and acetylthienone give salts with phosphoric acid and acetophenone, *p*-acetyltoluene, *p*-acetyethylbenzene, acetyl- $\psi$ -cumene, and acetylanisole salts with arsenic acid. *o*- and *m*-Acetyltoluenes and acetyl-*p*-cymene fail to give such derivatives.

Aliphatic aromatic ketones in which the alkyl radicle combined with the carbonyl group is greater than  $\text{CH}_3$ , do not, as a rule, form salts with phosphoric acid; this was found to hold in the case of

propionylbenzene, *p*-propionyltoluene, butyryl- and isobutyryl-benzene, butyryl-*m*-xylene, *p*-propionylethylbenzene, propionylanisole, propionylphenetole, and butyrylphenetole. Propionyl  $\psi$ -cumene is an exception, as it gives a well-defined salt. W. A. D.

**Action of Hydroxylamine on some Halogen Derivatives of Acetophenone.** By A. COLLET (*Bull. Soc. Chim.*, 1902, [iii], 27, 539—543).— $\beta$ -*p*-Dichloroacetophenoneoxime,  $\text{CH}_2\text{Cl}\cdot\text{C}(\text{NOH})\cdot\text{C}_6\text{H}_4\text{Cl}$ , obtained by the action of hydroxylamine hydrochloride on the corresponding ketone in methyl alcoholic solution, forms slender, white needles which melt at  $100\cdot5$ — $101^\circ$  and are insoluble in water, sparingly soluble in cold, more so in hot light petroleum or carbon disulphide. When heated on the water-bath with concentrated sulphuric acid, it is converted into *chloroacetyl-p-chloroanilide*,  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$ .  $\beta$ -*Bromo-p-chloroacetophenoneoxime*, obtained in a similar manner to the preceding oxime, separates from its solution in carbon disulphide in colourless, silky needles, soft to the touch, which melt at  $106\cdot5^\circ$  and are soluble in hot light petroleum. When heated with concentrated sulphuric acid, it yields *bromoacetyl-p-chloroanilide*.

$\beta$ -*Chloro-p-bromoacetophenoneoxime* forms very light, slender, colourless, silky needles which melt at  $115^\circ$ . Sulphuric acid converts it into *chloroacetyl-p-bromoanilide*, which melts at  $180$ — $181^\circ$ .  $\beta$ -*p-Dibromoacetophenoneoxime* forms lustrous, colourless needles melting at  $115^\circ$ . The corresponding anilide melts at  $169$ — $170^\circ$ .  $\beta$ -*Dibromo-p-chloroacetophenoneoxime* forms small, colourless crystals, which do not melt sharply, fusion taking place at  $102$ — $108^\circ$ ; it is very soluble in methyl or ethyl alcohol, and in benzene, less so in carbon disulphide. The corresponding *dibromoacetyl-p-chloroanilide* melts at  $162$ — $163^\circ$ .  $\beta\beta$ -*p-Tribromoacetophenoneoxime* forms colourless crystals melting at  $111$ — $112^\circ$ , readily soluble in methyl or ethyl alcohol or in benzene, carbon disulphide, or light petroleum. *Dibromoacetyl-p-bromoanilide* melts slightly above  $170^\circ$ . *p-Chlorophenylglyoxime*,



obtained by the action of hydroxylamine hydrochloride on dibromoethyl-*p*-chlorophenylketone, melts at  $198$ — $199^\circ$ , and crystallises from alcohol in light, slender, colourless needles, insoluble in water, very soluble in methyl or ethyl alcohol, and in ether, sparingly so in benzene. *p-Bromophenylglyoxime* is a colourless, crystalline powder melting at  $171$ — $172^\circ$ ; it is insoluble in water, very soluble in methyl or ethyl alcohol, soluble in boiling benzene.

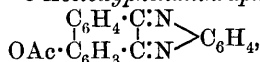
For purposes of identification, the author has also prepared a number of the anilides described above by the action of the chloride of chloroacetyl and of bromoacetyl on *p*-chloroaniline or *p*-bromoaniline, the reaction being moderated by dissolving the acid chloride in carbon disulphide. A. F.

**Ketones and Oximes containing a Tetrahydronaphthalene Nucleus.** By W. SCHARWIN (*Ber.*, 1902, 35, 2511—2515).—*Tetrahydronaphthyl methyl ketone*, obtained by the action of acetyl chloride on tetrahydronaphthalene in presence of aluminium chloride, is a

colourless, aromatic liquid which boils at 152° under 12 mm. pressure. The only *oxime* obtained crystallises in colourless needles, melts at 106°, and has the configuration  $\begin{array}{c} \text{C}_{10}\text{H}_{11}\cdot\text{C}\cdot\text{Me} \\ | \\ \text{HO}\cdot\text{N} \end{array}$ , which is shown by its transformation into aceto- $\beta$ -tetrahydronaphthalide.

*Phenyl tetrahydronaphthyl ketone* is a viscous, yellow liquid which boils at 222—223° under 12 mm. pressure. The crude *oxime* can be separated by fractional crystallisation from acetic acid and alcohol into the less soluble *oxime*,  $\begin{array}{c} \text{C}_{10}\text{H}_{11}\cdot\text{C}\cdot\text{Ph} \\ | \\ \text{HO}\cdot\text{N} \end{array}$ , which melts at 142°, and can be transformed into *benzoyl- $\beta$ -tetrahydronaphthalide* (m. p. 166—167°), and its *stereoisomeride*,  $\begin{array}{c} \text{C}_{10}\text{H}_{11}\cdot\text{C}\cdot\text{Ph} \\ | \\ \text{N}\cdot\text{OH} \end{array}$ , which melts at 116°, and can be transformed into the *anilide* of tetrahydronaphthoic acid (m. p. 153°).  
R. H. P.

**Phenanthrene. II.** By ALFRED WERNER [and, in part, TOBIAS FREY, A. GROB, H. HEIL, JOHANNES KUNZ, MAX KUNZ, BERNH. LÖWENSTEIN, ADOLF NEY, K. REKNER, ADOLF SCHERRER, H. SCHWABACHER, and AD. WACK] (*Annalen*, 1902, 322, 135—173. Compare this vol., i, 437).—3-Acetoxyphenanthraquinone,  $\text{C}_{14}\text{H}_7\text{O}_2\cdot\text{OAc}$ , produced by oxidising 3-phenanthryl acetate with chromic acid in glacial acetic acid solution, crystallises from this solvent in golden-yellow needles melting at 199—201°. 3-Acetoxyphenanthraphenazine,



obtained by condensing the preceding compound dissolved in glacial acetic acid with *o*-phenylenediamine in alcoholic solution, crystallises from alcohol or benzene in yellow needles melting at 223—225°. The

*phenylhydrazone*,  $\begin{array}{c} \text{C}_6\text{H}_4\cdot\text{CO} \\ | \\ \text{OAc}\cdot\text{C}_6\text{H}_3\cdot\text{C}\cdot\text{N}\cdot\text{NHPh} \end{array}$ , of this quinone is obtained in red needles with a green reflex; it is readily soluble in the ordinary organic solvents and melts at 207—209°.

3-Hydroxyphenanthraquinone may be prepared either by hydrolysing the preceding acetyl compound or by treating 3-aminophenanthraquinone with sodium nitrite in the presence of dilute sulphuric acid; it sublimes in brick-red needles and has no definite melting point. The hydrolysis is effected by dissolving the acetyl compound in concentrated sodium hydrogen sulphite solution saturated with ether; the latter solvent is necessary, otherwise the quinone does not pass into solution. The hydroxy-derivative is separated by distilling off the ether and acidifying the residual solution with a mineral acid; it is shown to be identical with the substance obtained from 3-aminophenanthraquinone by acetylating the latter hydroxyquinone with acetic anhydride; the product crystallises in the characteristic golden-yellow needles melting at 200—201°.

3-Hydroxyphenanthraphenazine,  $\begin{array}{c} \text{C}_6\text{H}_4\cdot\text{C}\cdot\text{N} \\ | \\ \text{OH}\cdot\text{C}_6\text{H}_3\cdot\text{C}\cdot\text{N} \end{array} > \text{C}_6\text{H}_4$ , produced by hydrolysing the corresponding acetyl derivative with alcoholic potass-

ium hydroxide solution, is insoluble in the ordinary organic solvents and separates from pyridine, on adding water, as a yellow, crystalline powder infusible below  $340^{\circ}$ . 3-Hydroxyphenanthraquinone phenylhydrazone, obtained in a similar manner from the phenylhydrazone of the acetoxyquinone, crystallises from glacial acetic acid in red needles and melts at  $235-238^{\circ}$ ; it is readily soluble in the ordinary organic solvents.

3-Benzoyloxyphenanthraquinone,  $C_{14}H_7O_2 \cdot OBz$ , obtained by oxidising 3-phenanthryl benzoate with chromic acid, crystallises from glacial acetic acid in lustrous, yellow needles and melts at  $224-226^{\circ}$ ; the corresponding phenazine is an amorphous, yellow powder melting at  $234-236^{\circ}$ .

3-Benzenesulphophenanthraquinone,  $C_{14}H_7O_2 \cdot O \cdot SO_2Ph$ , produced by the oxidation of 3-phenanthrylbenzenesulphonate, crystallises from glacial acetic acid in dark-yellow leaflets melting at  $216-218^{\circ}$ .

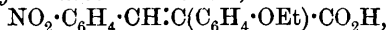
3-Methoxyphenanthraquinone,  $C_{14}H_7O_2 \cdot OMe$ , results from the oxidation of 3-phenanthryl methyl ether with chromic acid; it crystallises from glacial acetic acid in orange-yellow needles and melts at  $204-205^{\circ}$ . The yield is small owing to the formation of a dimethoxydiketodiphenanthryl. This quinone is undoubtedly identical with Pschorr's 3-methoxyphenanthraquinone which melts at  $206^{\circ}$  (Abstr., 1900, i, 233).

3-Ethoxyphenanthraquinone crystallises from glacial acetic acid or alcohol in orange-coloured needles and melts at  $207-208^{\circ}$ ; it may be obtained either by oxidising phenanthryl ethyl ether or by condensing *p*-ethoxyphenyl-*o*-aminocinnamic acid; the starting point in the latter synthesis being *p*-hydroxybenzyl cyanide.

*p*-Ethoxybenzyl cyanide,  $OEt \cdot C_6H_4 \cdot CH_2 \cdot CN$ , produced by alkylating the hydroxy-compound with ethyl iodide in alcoholic potassium hydroxide solution, crystallises from dilute alcohol in white leaflets melting at  $47^{\circ}$ .

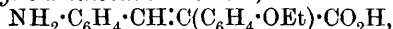
*p*-Ethoxyphenylacetic acid,  $OEt \cdot C_6H_4 \cdot CH_2 \cdot CO_2H$ , is obtained either by hydrolysing the nitrile with alcoholic potassium hydroxide solution or by the direct action of ethyl sulphate on the hydroxy-nitrile in the presence of excess of the alkali hydroxide; the substance is liberated by mineral acids and crystallises from dilute alcohol or hot water in colourless leaflets melting at  $89^{\circ}$ ; when prepared according to the second process, it is accompanied by a certain amount of its amide,  $OEt \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot NH_2$ , a compound crystallising from water in white leaflets melting at  $184^{\circ}$ .

*α-p*-Ethoxyphenyl-*o*-nitrocinnamic acid,



prepared by condensing *o*-nitrobenzaldehyde with the sodium salt of the preceding acid in the presence of excess of acetic anhydride at  $130-150^{\circ}$ , is extracted with sodium hydroxide solution, reprecipitated by mineral acids, and recrystallised from toluene or glacial acetic acid, forming amber-coloured, prismatic crystals melting at  $158^{\circ}$ . Although insoluble in water, it readily dissolves in the ordinary organic solvents excepting light petroleum.

*α-p*-Ethoxyphenyl-*o*-aminocinnamic acid,



obtained by reducing the preceding compound with ferrous sulphate in ammoniacal solution, separates on adding dilute hydrochloric acid to the filtered solution in two modifications, one being white and the other yellow. The former variety is always accompanied by the latter and both forms melt at  $189^{\circ}$ . The acid is insoluble in water or dilute mineral acids, but readily dissolves in solutions of the alkali hydroxides or in the ordinary organic solvents. When treated with sodium nitrite in the presence of dilute sulphuric acid, a diazo-derivative is produced which on adding copper powder undergoes condensation to yield *3-ethoxyphenanthrene-10-carboxylic acid*; this product crystallises from alcohol in greyish-white leaflets melting at  $206^{\circ}$ , and furnishes 3-ethoxyphenanthraquinone on oxidation with chromic acid.

3-Hydroxyphenanthraquinone, on treatment with excess of nitric acid at  $50^{\circ}$ , yields *mononitro-3-hydroxyphenanthraquinone*, a compound crystallising in yellow needles and melting at  $259-260^{\circ}$ ; 3-methoxyphenanthraquinone also yields a nitro-compound which, however, was not obtained pure; these nitro-derivatives give rise to amines on reduction. 3-Acetoxyphenanthraquinone, when nitrated, furnishes two nitro-derivatives, a *mononitro*-compound crystallising in golden-yellow needles and melting at  $217^{\circ}$ , and a *dinitro*-compound melting at  $263-265^{\circ}$ . When the acetoxyquinone is treated with nitric acid at the boiling point, a third nitro-product is formed which crystallises in pale yellow needles and melts at  $200-201^{\circ}$ .

2-Hydroxyphenanthraquinone, obtained by oxidising 2-phenanthryl acetate with chromic acid, extracting the product with sodium hydrogen sulphite, and decomposing the additive compound with warm dilute sulphuric acid, crystallises from glacial acetic acid in slender, violet-black needles melting at  $280-283^{\circ}$ . This compound may also be produced in much better yield by the action of nitrous acid on 2-aminophenanthraquinone. 2-Acetoxyphenanthraquinone,  $C_{14}H_7O_2 \cdot OAc$ , results from the action of acetic anhydride on the hydroxyquinone at  $120-130^{\circ}$ ; it crystallises from light petroleum in needles or plates melting at  $215-216^{\circ}$ .

2-Benzoyloxyphenanthraquinone, prepared either by the oxidation of 2-phenanthryl benzoate or by subjecting the hydroxyquinone to the Schotten-Baumann reaction, crystallises from benzene in yellow needles melting at  $240-242^{\circ}$ .

2-Benzenesulphophenanthraquinone,  $C_{14}H_7O_2 \cdot O \cdot SO_2Ph$ , produced by a modification of the latter reaction, is a light-brown, uncrystallisable powder.

2-Phenanthryl methyl ether,  $C_{14}H_7O_2 \cdot OMe$ , readily obtained by methylating the hydroxy-compound with dimethyl sulphate in the presence of potassium hydroxide solution, crystallises from glacial acetic acid in dark red needles melting at  $170-171^{\circ}$ .

2-Phenanthryl ethyl ether,  $C_{14}H_7O_2 \cdot OEt$ , produced in a similar manner by the action of ethyl sulphate, crystallises in red leaflets and melts at  $160-161^{\circ}$ ; these ethers may also be prepared by the action of the corresponding alkyl iodides in the presence of the alcoholic sodium alkyl oxides, but only a very small amount of the methyl ether is thus obtained.

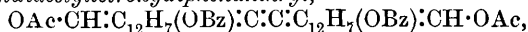
2-Methoxyphenanthraquinone, when distilled with soda-lime, gives

rise to 2-methoxyfluorenone,  $C_{14}H_{10}O_2$ , and 2-methoxyfluorene; the former crystallises in orange-yellow needles and melts at  $106-108^\circ$ ; these products were identified by comparison with specimens directly prepared from 2-hydroxyfluorenone and 2-hydroxyfluorene respectively.

*Bromophenanthraquinone*, prepared by oxidising dibromophenanthrene, crystallises from glacial acid in nodular aggregates melting at  $126^\circ$ ; the position of the bromine atom has not yet been determined.

In preparing 3-hydroxyphenanthraquinone from 3-benzoyloxyphenanthraquinone, a bye-product is obtained which does not dissolve in sodium hydrogen sulphite solution. This substance, *dibenzoyloxydiphenanthronylene*,  $CO \cdot C_{12}H_7(Obz) : C : C : C_{12}H_7(Obz) : CO$ , crystallises from glacial acetic acid in reddish-yellow needles melting at  $205-206^\circ$ .

*Dibenzoyldiacetyltetrazydiphenanthryl*,



obtained by reducing the preceding compound with zinc and hydrochloric acid and treating the unstable dihydric alcohol with acetic anhydride, crystallises from glacial acetic acid in lustrous, white needles melting at  $225-226^\circ$ .  
G. T. M.

**Dibromoxyloquinhydrone.** By G. TEICHER (Ber., 1902, 35, 2303—2304).—The dark coloured substance melting at  $169-170^\circ$  obtained by Auwers and Sigel (this vol., i, 216) by the oxidation of halogen derivatives of  $\psi$ -phenols, which was thought by them to be dibromoxyloquinone, is in reality *dibromoxyloquinhydrone*. This compound can be prepared by the union of the quinone with the corresponding quinol, and is converted by oxidation into the quinone melting at  $184^\circ$ , by reduction into the quinol melting at  $174-175^\circ$ .

A. H.

**Preparation of Anthrachryson.** By W. HOHENEMSER (Ber., 1902, 35, 2305—2306).—The disulphobenzoic acid requisite for this preparation is best obtained by heating benzoic acid with 4.5 parts of fuming sulphuric acid containing 70 per cent. of anhydride in sealed tubes for 3 hours at  $250^\circ$  (compare Barth and Senhofer, *Annalen*, 1871, 159, 218). At  $100^\circ$ , the fuming sulphuric acid only produces monosulphobenzoic acid. The condensation to anthrachryson is effected by heating the disulpho-acid at  $100^\circ$  for 1 hour with 10 parts of pure sulphuric acid.  
A. H.

**Isomerism in the Benzylidenementhones, and the Preparation of an  $\alpha$ -Methyl- $\delta$ -isopropyladipic Acid identical with Dihydrocamphoric Acid.** By CAMILLE MARTINE (*Compt. rend.*, 1902, 134, 1437—1439).—From the oily products obtained in the preparation of benzylidene-menthone (Abstr., 1901, i, 599), two substances can be isolated, which appear to be two isomeric *benzylidenementhones*; the one, which is formed in much larger quantity, crystallises in plates melting at  $51^\circ$ , and has  $[\alpha]_D - 185.50'$ ; its *oxime* crystallises in slender needles melting at  $172^\circ$ . The other forms long needles melting at  $47^\circ$ , and has  $[\alpha]_D - 258.50'$ ; its *oxime* melts at  $153^\circ$ .

$\alpha$ -Methyl- $\delta$ -isopropyladipic acid,  $CO_2H \cdot CHMe \cdot C_2H_4 \cdot CHPr^B \cdot CO_2H$ , is obtained, together with benzoic acid, when the benzylidenementhone

(m. p.  $51^{\circ}$ ) is oxidised with dilute aqueous permanganate; it melts at  $105^{\circ}$  and is inactive to polarised light; when boiled with acetic anhydride, it gives an anhydride,  $C_{10}H_{16}O_3$ , which, on prolonged heating, loses carbon dioxide and is converted into a *ketone*,  $C_9H_{16}O$ , having the odour of menthone and boiling at  $180$ — $181^{\circ}$ ; the *semicarbazone* of the latter melts at  $205^{\circ}$ . The methylisopropyladipic acid is shown to be identical with the dihydrocamphoric acid obtained by Crossley and Perkin (Trans., 1898, 73, 23) by fusing camphoric acid with potassium hydroxide. The ketone just mentioned is probably  $\alpha$ -methyl- $\delta$ -isopropylketocyclopentane. K. J. P. O.

**Xanthamides of the Terpene Series.** By L. TSCHUGAEFF (*Ber.*, 1902, 35, 2473—2483. Compare Abstr., 1900, i, 129, 352; 1901, i, 38).—Although the methyl xanthic esters of the alcohols,  $C_nH_{2n+1}OH$ , decompose at a low temperature into the corresponding olefine, carbon oxysulphide, and methyl mercaptan, this is not true of the esters of these alcohols with ordinary acids. Thus *menthyl oxalate*, which melts at  $67$ — $68^{\circ}$  and has  $[\alpha]_D - 101.5^{\circ}$  in benzene solution ( $c = 1.902$ ), can be distilled without decomposition at  $225^{\circ}$  under a pressure of 12 mm., and can be heated to a much higher temperature without decomposing. The same is true of *menthyl carbonate*, *menthyl succinate*, *menthyl acetate*, which boils at  $227^{\circ}$ , *diphenylmenthylurethane*, &c. Menthyl benzoate is also very stable, but after being heated for 10 hours at  $250^{\circ}$  in a sealed tube, decomposes to a small extent, yielding menthene and benzoic acid.

It has been shown previously that the dixanthides are readily decomposed in the same way as xanthic esters, and this observation has now been extended to the xanthamides, which are obtained by the action of alcoholic ammonia on the corresponding xanthic methyl esters (Debus).

*Menthylxanthamide*,  $C_{10}H_{19}O \cdot CS \cdot NH_2$ , crystallises in small needles melting at  $144$ — $145^{\circ}$ , is almost insoluble in water, and has the normal molecular weight. It has  $[\alpha]_D - 115.9^{\circ}$  in toluene ( $c = 4.9927$ ), but this varies both with the concentration and with the nature of the solvent. The crystals show triboluminescence. When it is heated, it commences to decompose at about  $200^{\circ}$  and yields menthene, carbon oxysulphide, and other products. This decomposition is typical for all the xanthamides examined.

*Bornylxanthamide*,  $C_{10}H_{17}O \cdot CS \cdot NH_2$ , was prepared in both optical forms. These crystallise in long prisms, show triboluminescence, and melt at  $125$ — $126^{\circ}$ . The *d*-amide has in benzene  $[\alpha]_D + 18.95^{\circ}$  ( $c = 6.4053$ ); the *l*-amide has  $[\alpha]_D - 18.13^{\circ}$  ( $c = 5.481$ ). These rotations are exceptional in being lower than those of the corresponding alcohols. *r*-*Bornylxanthamide* melts at  $134.5$ — $135.5^{\circ}$ , and does not show triboluminescence.

*1-Fenchylxanthamide*,  $C_{10}H_{17}O \cdot CS \cdot NH_2$ , crystallises in nacreous plates melting at  $129$ — $130^{\circ}$ , and has  $[\alpha]_D - 78.51^{\circ}$  ( $c = 10.402$ ) in benzene. Methyl dihydrocarvylxanthate yields with ammonia a mixture of two amides, derived from two isomeric dihydrocarveols. The *a*-amide forms large crystals melting at  $62.5$ — $63.5^{\circ}$ , and has  $[\alpha]_D + 135.33^{\circ}$  ( $c = 9.226$ ) in benzene. The dihydrocarveol obtained from it by hydrolysis boils at  $222.5$ — $223^{\circ}$  and has



$[\alpha]_D + 33.86^\circ$ , sp. gr. 0.9204 at  $20^\circ/4^\circ$ , and  $n_D$  1.47818 at  $20^\circ$ . The  $\beta$ -amide could not be obtained pure, but the crude liquid gave on hydrolysis a dihydrocarveol boiling at  $120^\circ$  under 20 mm. pressure;  $[\alpha]_D + 7.64^\circ$ , sp. gr. 0.9266 at  $20^\circ/4^\circ$ ,  $n$  1.48087 at  $20^\circ$ . Thioamides and thiocarbamides give a deep blue coloration when they are heated with a few drops of benzophenone chloride, and can readily be recognised by this reaction.

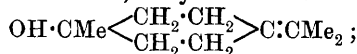
A. H.

$\Delta^{8:9}$ Terpen-1-ol: a New Terpeneol Melting at  $32^\circ$ . By KARL STEPHAN and J. HELLE (*Ber.*, 1902, 35, 2147—2158).—Liquid terpeneol, when distilled under diminished pressure, yields two principal fractions, the first boiling at  $212$ — $215^\circ$  under the ordinary pressure, and having a sp. gr. 0.930 at  $15^\circ$ , and the second boiling at  $218$ — $220^\circ$ , and having a sp. gr. 0.940 at  $15^\circ$ . Both these products solidify on cooling, the second fraction yielding after repeated crystallisation from alcohol, the well-known terpeneol melting at  $35$ — $36^\circ$ , whilst the first fraction furnishes a new isomeride melting at  $32$ — $33^\circ$ .

The terpeneol melting at  $35$ — $36^\circ$  boils at  $98$ — $99^\circ$  under 10 mm., and at  $218.8$ — $219.4^\circ$  under 752 mm. pressure; it has a sp. gr. 0.939 at  $15^\circ/15^\circ$  and 0.935 at  $20^\circ/20^\circ$ ,  $n_D$  at  $20^\circ$  is 1.48132. Its *phenylurethane*,  $C_{17}H_{23}O_2N$ , melts at  $112$ — $113^\circ$ ; the *nitrosochloride* melts at  $103^\circ$ , and on treatment with piperidine readily yields the *nitrolepiperidide*, melting at  $159^\circ$ . On oxidation with dilute permanganate solution, trihydroxyhexahydrocymene is produced, and this, on further treatment with chromic acid, gives rise to the keto-lactone,  $C_{10}H_{16}O_3$ , melting at  $62$ — $63^\circ$ . The new terpeneol crystallises in needles, and boils at  $90^\circ$  under 10 mm., and at  $209$ — $210^\circ$  under 752 mm. pressure; it has sp. gr. 0.923 at  $15^\circ/15^\circ$ , and 0.919 at  $20^\circ/20^\circ$ ,  $n_D$  at  $20^\circ$  being 1.47470.

The *phenylurethane* melts at  $85^\circ$ ; the *nitrosochloride* melts at  $102$ — $103^\circ$ , but does not readily yield a nitrolepiperidide. This terpeneol is not readily acetylated, a fact which points to its being a tertiary alcohol.

Terpin,  $OH \cdot CMe \langle \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} \rangle CH \cdot CMe_2 \cdot OH$ , on dehydration, may give rise to four isomeric terpeneols, the isomeride melting at  $35^\circ$  being represented by the formula  $CMe \langle \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH - CH_2 \end{smallmatrix} \rangle CH \cdot CMe_2 \cdot OH$ . To the compound melting at  $60$ — $70^\circ$ , Baeyer ascribes the constitution

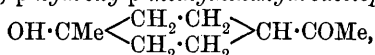


the remaining formulæ,  $CH_2 : C \langle \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} \rangle CH \cdot CMe_2 \cdot OH$  and  $OH \cdot CMe \langle \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} \rangle CH \cdot CMe : CH_2$ , are available for the new substance, and the latter of these is considered to be the more probable, owing to the behaviour of the alcohol towards oxidising agents.

$\Delta^{8:9}$ Terpen-1-ol, when treated with 1 per cent. potassium permanganate solution, yields the trihydric alcohol, 1:8:9-trihydroxyhexahydrocymene,  $OH \cdot CMe \langle \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} \rangle CMe(OH) \cdot CH_2 \cdot OH$ , which crystallises from ethyl acetate or benzene in prisms melting at

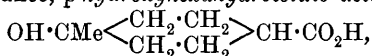
118—118.5°; this product is soluble in warm water, the solution having a bitter taste. The trihydric alcohol, on oxidation with chromic acid, furnishes a ketone, *p*-methyltetrahydroacetophenone,  $\text{CMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH} \cdot \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{COMe}$ , this product boiling at 68.5—70° under 4 mm. pressure, and having sp. gr. 0.9435 and  $n_D$  1.47421 at 15°. The observed molecular refraction points to its containing one ethylene linking. The *semicarbazone*,  $\text{C}_{10}\text{H}_7\text{ON}_3$ , of the ketone crystallises in white leaflets and melts at 160°.

The oxidation of the trihydric alcohol also leads to the production of another ketone, *p*-hydroxy-*p*-methylhexahydroacetophenone,



a compound boiling at 140—145° under 19 mm. pressure, and having a sp. gr. 1.023 and  $n_D$  1.47548 at 20°; the corresponding *semicarbazone*,  $\text{C}_{10}\text{H}_{19}\text{O}_2\text{N}_3$ , melts at 195—196°.

An acidic substance, *p*-hydroxyhexahydro-toluic acid,



melting at 153°, is obtained by treating the hydroxy-ketone with an alkaline solution of sodium hypobromite, bromoform being simultaneously produced. This acid is also formed by treating the trihydric alcohol with bromine and sodium hydroxide, only in this case the other product is tetrabromomethane. The acid contains hydroxyl, and yields with phenylcarbimide a phenylurethane melting at 162—163°; it forms a lactone,  $\text{C}_8\text{H}_{12}\text{O}_2$ , when distilled under the ordinary pressure; this product crystallises in serrated leaflets and melts at 68—69°. When, however, the hydroxy-acid is heated with 20 per cent. sulphuric acid, it loses the elements of water and becomes converted into tetrahydro-*p*-toluic acid (m. p. 98°), this substance being also produced by the action of sodium hypobromite on the unsaturated ketone. Warm concentrated sulphuric acid brings about an elimination of both water and hydrogen from the hydroxy-acid, giving rise to *p*-toluic acid.

G. T. M.

**Crystallographic Properties of Benzylidene-, Methylsalicylidene-, Ethylsalicylidene-, and Anisylidene-camphor, and of their Reduction Products.** By JULES MINGUIN (*Bull. Soc. Chim.*, 1902, [iii], 27, 544—549).—Dextro- and lævo-benzylidenecamphor crystallise in the forms of the rhombic system; the racemic compound, however, in the monoclinic system. In the case of anisylidenecamphor, the active as well as the racemic forms crystallise in rhombic prisms. *d*-Methylsalicylidenecamphor, and *d*-ethylsalicylidenecamphor both belong to the monoclinic system, the former crystallising in prisms, the latter in plates. Benzyl-, anisyl-, and ethyl-saligenylcamphor all crystallise in the rhombic system.

A. F.

**Some Reactions of Fenchone.** By E. TARDY (*Bull. Soc. Chim.*, 1902, [iii], 27, 603—606).—If molecular proportions of a phenol and fenchone, previously heated to 60°, are mixed, the temperature rises and the resulting liquid has a higher rotatory power than fenchone;

the compound formed dissociates under the influence of solvents.  $\alpha$ -Naphtholfenchone, obtained by mixing the two components at the ordinary temperature, forms white, flat, acicular crystals melting at  $51^{\circ}$ ;  $\beta$ -naphtholfenchone forms large prisms melting at  $57^{\circ}$ . Both compounds readily dissociate, and when exposed to the air the fenone passes off, leaving the naphthols behind. Thymol, guaiacol, eugenol, and resorcinol also appear to form compounds with fenchone, the latter phenol combining with one or with two molecules of fenchone. They are all non-crystallisable.

Chloral also dissolves in fenchone and a crystalline compound can be obtained melting between  $25^{\circ}$  and  $30^{\circ}$ .

Fenchone also dissolves nitrocellulose, yielding a gelatinous mass which dissolves in ether; even a 10 per cent. solution of fenchone in alcohol dissolves nitrocellulose, forming a sort of collodion. A. F.

**Some Further Constituents of the Essential Oil of *Kaempferia Galanga*.** By PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 4, 618—620. Compare Abstr., 1900, i, 677).—Besides ethyl *p*-methoxycinnamate, previously found in the essential oil of *Kaempferia Galanga*, ethyl cinnamate has also been detected. Its isolation is difficult on account of the presence of an indifferent substance which congeals at about  $10^{\circ}$ . The fraction of the oil boiling at  $155$ — $165^{\circ}$  under 30 mm. pressure was treated with 80 per cent. alcohol, which dissolved out the ethyl cinnamate. The insoluble residue, on repeated treatment with alcoholic potassium hydroxide, gave a liquid which was only slightly optically active and which became tinged with green on treatment with bromine. On purification by means of bromine, an inactive, colourless, odourless hydrocarbon of the formula  $C_{15}H_{32}$  boiling at  $267.5^{\circ}$  under 738 mm. pressure was obtained which solidifies in a freezing mixture and melts at  $10^{\circ}$ . It has a sp. gr. 0.766 at  $26^{\circ}$  and its properties agree closely with those of *n*-pentadecane described by Krafft (Abstr., 1882, 1272).

J. McC.

**Solubility of certain Fresh Resins.** By CH. COFFIGNIER (*Bull. Soc. Chim.*, 1902, [iii], 27, 549—555).—The solubility of a number of resins has been determined both by enclosing the resin in a cartridge of filter paper and extracting with a Soxhlet apparatus, and by boiling a weighed quantity of resin with a known volume of solvent. The chief results are as follows:—Dammar: completely soluble in oil of turpentine, but a small portion separates out when kept for some months; in ethyl alcohol at  $95^{\circ}$ , 28.6 per cent. insoluble; in amyl alcohol, 13 per cent. insoluble; completely soluble in chloroform, in hot benzene (the solution becomes slightly turbid on cooling), or in carbon tetrachloride; in ether, about 3.5 per cent. remains undissolved, and in amyl acetate about 2.73 per cent.; completely soluble in boiling amyl acetate. Sandarac: 73—82 per cent. insoluble in oil of turpentine; completely soluble in oil of spike, oil of rosemary, oil of cajeput, ethyl alcohol, or in amyl alcohol; 55 per cent. insoluble in chloroform, 67—85 per cent. insoluble in benzene; completely soluble in ether, in acetone, or in amyl acetate; 78 per cent. insoluble in

carbon tetrachloride. Mastic: completely soluble in oil of turpentine; 36—37 per cent. insoluble in ethyl alcohol; completely soluble in amyl alcohol, benzene, chloroform, ether, carbon tetrachloride (hot), or amyl acetate (hot); 9.5 per cent. insoluble in acetone. A. F.

**White Peru Balsam.** By A. BILTZ (*Chem. Zeit.*, 1902, 26, 436).—On pouring white peru balsam into absolute alcohol, a white, brittle substance is obtained which melts at 120—130° and is soluble in benzene, ethyl acetate, or chloroform, insoluble in alcohol, ether, water, or alkalis. After removal of the alcohol, solution of the balsam in ether, and treatment with sodium carbonate solution to remove cinnamic acid, there separates a wax-like mass which crystallises from dilute alcohol in needles and melts at 260°. On treatment of the ethereal solution with 1 per cent. aqueous potassium hydroxide and acidification of the alkaline extract, there is formed a brownish-yellow precipitate which melts at about 100°. The remainder of the balsam is hydrolysed by alcoholic potassium hydroxide and distilled with steam. The oil so obtained is separated by fractional distillation under reduced pressure into cinnamyl alcohol and a colourless oil, probably of the formula  $C_{20}H_{30}O$  or  $C_{20}H_{28}O$ , which has a pleasant odour, boils at 112° under 10 mm. pressure, has a sp. gr. 0.9433 at 17.5°, and on gentle oxidation yields benzaldehyde. The residue from the steam distillation is principally cinnamic acid. G. Y.

**New Glucoside, Aucubin, contained in the Seeds of Aucuba Japonica.** By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1902, 134, 1441—1443).—In order to extract the glucoside, *aucubin*, from the seeds of *Aucuba japonica*, the latter in a fresh state, are extracted with boiling 90 per cent. alcohol, into which passes the glucoside together with a relatively large quantity of sucrose. After completely distilling off the alcohol, the residue is diluted with water, and yeast is added to destroy the sugar. The glucoside is isolated by evaporating to dryness and crystallising the residue from alcohol; it forms tufts of elongated crystals melting at 181°, and has  $[\alpha]_D - 173.1^\circ$ . Aucubin does not contain nitrogen or reduce Fehling's solution; it is hydrolysed by emulsin or by dilute sulphuric acid, forming dextrose, a substance with a penetrating odour and a brown principle insoluble in water.

K. J. P. O.

**Researches on the Arrow Poisons from German East Africa.** By LUDWIG BRIEGER and G. DIESSELHORST (*Ber.*, 1902, 35, 2357—2359).—The arrow poison used by the Wapogorros, a tribe inhabiting the Ulunga plain in the south-west of German East Africa, contains an active principle which is first extracted with water, and then, after successive treatment with lead acetate and hydrogen sulphide, is removed by absolute alcohol from the residue left on evaporation. The solvent is again distilled off and the residue dissolved in water. A crystalline glucoside separates, which melts at 185—187° and contains C=56.01; H=7.59 per cent.; it is extremely poisonous, the lethal dose for a rabbit being 0.0005 gram per kilogram; the action of the drug resembles that of *Digitalis*. The mother liquor still possesses toxic

properties, and yields another crop of crystals; these melt at 175—181°, and differ somewhat in composition for the first substance (C=57·11; H=7·89). In all probability, this poison contains a mixture of two poisonous glucosides, one of which is found in the poison employed by the Wakambas. The final mother liquors from the crystalline glucosides contain an amorphous glucoside, which, however, is non-poisonous. The communication contains a tabulated comparison of the arrow poisons employed by the tribes of German East Africa.

G. T. M.

**Theory of Dyeing.** By ROBERT GNEHM and FELIX KAUFLEDER (*Zeit. angew. Chem.*, 1902, 15, 345—348).—The barium salt of chrysophenin was obtained by boiling the free acid with barium chloride as a brown, amorphous powder; in boiling water, it is soluble to the extent of 0·095 per cent. The barium salt of benzopurpurin is soluble to the extent of 0·045 per cent. Cotton wool becomes coloured when immersed in solutions of these salts, and it has been proved that the salt (not the free acid) is absorbed. Absorption of salt has also been proved in the case of the corresponding sodium salts. Benzopurpurin can also be absorbed by cotton directly, although it is only soluble to the extent of about 0·001 per cent. Wool dyed with either the salt or the free acid may be extracted with water or salt solutions until there remains only a very small quantity of dye on the fibre. It is concluded that the dyeing is complete when equilibrium has been established between the inner and outer spaces of the cells. The results obtained are in good agreement with the theory proposed by Weber (*Färberzeit.*, 1894, 202), but the authors insist that the conclusions can only be applied to the class of dyes investigated and may not be extended to the explanation of all dyeing processes.

Lanuginic acid (Knecht and Appleyard, *Abstr.*, 1889, 869) is not homogeneous, as has been proved by dialysis; it contains an appreciable quantity of a colloidal substance.

J. McC.

**Theory of the Dyeing Process.** By GEORG VON GEORGIEVICS (*Chem. Zeit.*, 1902, 26, 129—131).—An account, historical and critical, of the various papers published since 1894 on the theory of dyeing, which cannot be briefly abstracted.

K. J. P. O.

**Theory of the Dyeing Process.** By P. D. ZACHARIAS (*Chem. Zeit.*, 1902, 26, 289—291).—The author draws attention to the fact that von Georgievics (preceding abstract) has misrepresented the theory of dyeing put forward by him (*Färber-Zeitung*, 1901, No. 10, 11).

K. J. P. O.

**Theory of Dyeing.** By GEORG VON GEORGIEVICS (*Chem. Zeit.*, 1902, 26, 371).—A reply to Zacharias' criticism of the author's previous paper (compare preceding abstracts).

K. J. P. O.

**Criticism of the Dyeing-Theory of P. D. Zacharias.** By RUDOLF WEGSCHEIDER (*Chem. Zeit.*, 1902, 26, 372).—Zacharias' mathematical treatment of the theory of dyeing is shown to be erroneous (compare preceding abstract).

K. J. P. O.

**Wool Mordants.** By G. EBERLE and FR. ULFFERS (*Chem. Zeit.*, 1902, 26, 406—407).—In answer to the criticism of von Georgievics (compare preceding abstracts), the authors have given a summary of their experimental investigation of the part played by the alkali salts usually added to the mordanting bath in the process of dyeing. It is found that these salts remove free acid which affects injuriously the development of a good colour. Thus only the alkali salts of weak acids are efficacious; the stronger the acid in the alkali salt, the less intense is the colour.  
K. J. P. O.

**Adjective Colouring Matters of the Benzaldehyde Green and Rosamine Groups.** By CARL LIEBERMANN (*Ber.*, 1902, 35, 2301—2303).—The substitution of protocatechuic aldehyde for benzaldehyde in the preparation of colouring matters from dimethylaniline and *m*-dimethylaminophenol leads to the production of substances which readily dye with mordants. The substance produced from dimethylaniline is violet blue and dyes cotton violet to blue with alumina, blackish violet with iron, mordants. The derivative of *m*-dimethylaminophenol is coloured red and dyes a violet red on alumina and a gray violet on iron. The change of colour from green to blue by the introduction of two hydroxyl groups into the compound has been observed previously.  
A. H.

[**Brazilin and Brazilein.**] By CARL SCHALL (*Ber.*, 1902, 35, 2306).—Brazilin becomes less soluble in acetic acid when it is preserved for a considerable time, and therefore a 10—16 per cent. solution in acetic acid should be used for the preparation of brazilein instead of a 30 per cent. solution. With brazilein, hydroxylamine in presence of hydrochloric acid yields a dioxime, in spite of the fact that hydroxylamine alone, as found by Herzig, reduces brazilein.  
A. H.

**Comparison of Phylloporphyrin and Mesoporphyrin.** By LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1902, 223—226).—Contrary to Nencki and Zaleski's statement (*Abstr.*, 1901, i, 434), the absorption spectrum of mesoporphyrin is found closely to resemble that of phylloporphyrin and not that of hæmatoporphyrin. After being treated with bromine, mesoporphyrin shows the absorption band in the extreme visible red, which is characteristic of phylloporphyrin but not of hæmatoporphyrin after similar treatment (compare *Trans.*, 1900, 77, 1091). Salts of hæmatoporphyrin dissociate electrolytically in aqueous solution; as a weaker base than phylloporphyrin, it requires a larger excess of free acid to prevent hydrolysis.  
G. Y.

**Absorption of Ultra Violet Rays by Bilirubin, Biliverdin, Urobilin, and Proteinchrome.** By L. BIER and LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1902, 230—232).—Contrary to what might be expected from the results obtained by Hartley (*Trans.*, 1888, 53, 641), the absorption spectra of bilirubin, biliverdin, urobilin, and proteinchrome show no characteristic bands in the ultra violet. The difference in behaviour of urobilin and of phylloporphyrin and

hæmatoporphyrin is explained by the supposition that the absorption of violet rays depends, not on the constitution of the nucleus forming the basis of complicated substances, but rather on the presence of certain atomic groupings, which may not be present in all derivatives of the same parent-substance.

Urobilin must differ constitutionally more from the chromogen of the blood colouring matter than the latter does from chlorophyll.

G. Y.

**Catechin.** By M. KARNOWSKI and JOSEF TAMBOR (*Ber.*, 1902, 35, 2408—2409).—The formulæ,  $C_{25}H_{24}O_{11}$  and  $C_{21}H_{21}O_7$ , assigned to pentacetyl catechin and acetyl catechin tetramethyl ether by Kostanecki and Tambor have been confirmed by determining the number of hydroxyl groups, and by molecular weight determinations from the boiling point of solutions in benzene. The mol. weight and the number of methoxyl groups of trimethyl catechone have also been found to be in agreement with the formula  $C_{18}H_{18}O_7$ .

*Nitrotrimethyl catechone*,  $C_{18}H_{17}O_9N$ , crystallises from alcohol in long, yellow needles, and melts at  $141^\circ$ , with liberation of gas.

T. M. L.

**Catechin.** By STANISLAUS VON KOSTANECKI and R. G. KREMBES (*Ber.*, 1902, 35, 2410—2411).—The mol. weight and number of methoxyl groups of catechin tetramethyl ether are in agreement with the formula  $C_{19}H_{23}O_6$ . The *monobromo*-derivative,  $C_{19}H_{21}BrO_6$ , crystallises from alcohol in needles which decompose with frothing at  $170^\circ$ ; its *acetyl* derivative,  $C_{21}H_{23}BrO_7$ , crystallises from much alcohol in silky, white needles, and melts (without frothing) at  $172^\circ$ .

T. M. L.

**Pyromucic Acid and isoPyromucic Acid.** Action of Phosphorus Pentachloride and Phosphorus Oxychloride. By G. CHAVANNE (*Compt. rend.*, 1902, 134, 1439—1441. Compare *Abstr.*, 1901, i, 649).—Pyromucic chloride, originally prepared by Liës-Bodart (*Annalen*, 1857, 100, 327) by the action of phosphorus pentachloride on pyromucic acid, crystallises in prisms melting at  $-2^\circ$ , and boiling at  $170^\circ$ ; with ammonia, aniline, &c., it forms the amide, anilide, &c.

When phosphorus pentachloride is added to a solution of *isopyromucic* acid in chloroform, or phosphoryl chloride is added to a suspension of sodium *isopyromucate* in the same solvent, a substance is obtained which appears to be *isopyromucyl* phosphate,  $PO(O\cdot C_5H_3O_2)_3$ ; it crystallises in prisms melting at  $138^\circ$ . When left in contact, or warmed, with water, or dissolved in moist solvents, it is converted into a *diisopyromucyl* phosphate,  $OH\cdot PO(O\cdot C_5H_3O_2)_2$ , which forms a crystalline powder containing  $1H_2O$  and melting at  $110$ — $112^\circ$ ; when anhydrous it melts at  $154^\circ$ . It behaves as a monobasic acid, and its neutral solution gives white precipitates with silver, lead, and bismuth salts. By warming with normal sulphuric acid, it is hydrolysed to the mono-ester,  $PO(OH)_2\cdot O\cdot C_5H_3O_2$ .

Attention is drawn to the fact that *isopyromucic* acid differs from its isomeride by giving a green colour with ferric chloride; and it is suggested that the *iso*-acid possesses phenolic or enolic characters.

K. J. P. O.

**Products of the Decomposition of *d*-Lupanine from *Lupinus Albus*.** By ARTURO SOLDANI (*Arch. Pharm.*, 1902, 240, 260—272. Compare Abstr., 1893, i, 739; 1896, i, 193; and Davis, Abstr., 1897, i, 174).—A further investigation has been made of the products obtained when *d*-lupanine,  $C_{15}H_{24}ON_2$ , is brominated in acetic acid solution and the resulting tetrabromo-additive compound boiled with alcohol. In addition to the bases,  $C_8H_{15}ON$  and  $C_7H_{11}ON$  (originally described as  $C_8H_{13}ON$  and  $C_7H_9ON$ ), a third base was isolated; its platinichloride has a golden lustre and apparently decomposes at 211—212° without melting. C. F. B.

**Oxidation of Morphine by the Extract of *Russula Delica*.** By J. BOUGAULT (*Compt. rend.*, 1902, 134, 1361—1363).—Oxymorphine hydrochloride is precipitated in a crystalline form from an aqueous solution of morphine hydrochloride treated with an excess of the extract of *Russula delica*, this decoction being produced by triturating the fresh fungus with a mixture of sand and dilute glycerol. The base oxymorphine isolated from its hydrochloride by sodium hydrogen carbonate is identical with the compound, known as  $\psi$ -morphine, dehydromorphine, or oxydimorphine, obtained by oxidising morphine with an alkaline solution of potassium ferricyanide (compare Polstorff, Abstr., 1880, 408). The base is very insoluble in chloroform, amyl alcohol, or ethyl acetate, these solvents taking up less than 0.005 per cent. of the substance; it is most conveniently dissolved in ammoniacal amyl alcohol. The optical rotation of the base is extremely variable in alkaline solution; the addition of sodium hydroxide causes the angle of rotation to diminish until a minimum is reached, beyond this point an increase of alkalinity augments the optical activity.

The salts of oxymorphine with the mineral acids are very sparingly soluble in water, and the base may be conveniently separated from morphine by means of the sulphates. The salts of oxymorphine with the organic acids are more soluble in water in presence of excess of the acid, but they do not dissolve in alcohol. Oxymorphine, dissolved in concentrated sulphuric acid and treated with a drop of dilute formaldehyde solution, develops a green coloration; under these conditions, morphine gives rise to a deep reddish-violet coloration. G. T. M.

**Pilocarpine. Constitution of the Alkaloid. II.** By ADOLF PINNER and RUDOLF SCHWARZ (*Ber.*, 1902, 35, 2441—2459. Compare this vol., i, 232; and Jowett, Trans., 1900, 77, 851; 1901, 79, 580, 1331).—It has been shown by Jowett (*loc. cit.*) that with silver oxide isopilocarpine methiodide yields a hydroxide which does not give precipitates with platinic chloride or picric acid until it has been boiled with hydrochloric acid. The authors point out that in the treatment with silver oxide the lactone ring, known to be present in pilocarpine and isopilocarpine-methiodide, has been opened, and that the compound obtained by Jowett was isopilocarpic acid methohydroxide,  $C_{11}H_{18}O_3N_2 \cdot CH_3 \cdot OH$ , and not isopilocarpine methohydroxide; and, further, on boiling this substance with acids, the lactone ring is again formed, isopilocarpine methochloride being produced, and now giving a platinichloride.



Since, by oxidation of pilocarpine or *isopilocarpine* with permanganate, homopilopie acid (of known constitution) is obtained (Jowett), the complex,  $\begin{array}{c} \text{CHEt} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{C} \\ \text{CO} \cdot \text{O} \cdot \text{CH}_2 \end{array}$ , must be present in the alkaloids; further,

it is suggested that the group  $\text{C}_2\text{H}_2\text{N} \cdot \text{NMe}$  which, in the oxidation, is converted into ammonia, methylamine, and carbon dioxide, forms part of a glyoxaline ring, and therefore that pilocarpine (or *isopilocarpine*) has the constitution  $\begin{array}{c} \text{CHEt} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{C} \cdot \text{NMe} \\ \text{CO} \cdot \text{O} \cdot \text{CH}_2 \quad \text{CH} - \text{N} \geq \text{CH} \end{array}$ .

Pilocarpine is found to behave as a glyoxaline derivative. It is shown that although methylglyoxaline is stable towards alkalis, methylglyoxaline-alkylhaloids are readily decomposed, yielding methylamine, the alkylamine, formic acid, and methyl alcohol. Pilocarpine and *isopilocarpine* behave in an exactly similar manner; they are stable towards alkalis, but their alkyl salts decompose easily, yielding, besides formic and homopilopie acids, methylamine and the alkylamine. Pilocarpine forms a substituted product with bromine, as do the glyoxalines, and not an additive product. Pilocarpine and the glyoxalines are readily oxidised by permanganate and hydrogen peroxide, but not by chromic acid. Again, benzoyl chloride reacts with glyoxaline, but not with methylglyoxaline, and pilocarpine also is not attacked by benzoyl chloride.

Pilocarpine and *isopilocarpine* cannot be stereoisomeric, as, when oxidised with chromic acid, the former yields pilocarpoeic acid,  $\text{C}_{11}\text{H}_{16}\text{O}_5\text{N}_2$ , whilst the latter is slowly broken up; also with bromine water quite different products are obtained.

Pilocarpine ethosulphate (from pilocarpine ethiodide and silver sulphate), pilocarpine propobromide and amylobromide were prepared, and their behaviour on boiling with 30 percent. potassium hydroxide studied, with the results previously described. The analogous decomposition of methylglyoxaline amylobromide, amyglyoxaline methiodide, and benzylglyoxaline methiodide was investigated.

When dibromopilocarpine or dibromo*isopilocarpine* is boiled with barium hydroxide, barium dibromo*isopilocarpate* is formed, from which the acid  $\text{C}_{11}\text{H}_{16}\text{O}_3\text{N}_2\text{Br}_2$  can be prepared; the latter crystallises in needles melting at  $120^\circ$  and losing water at  $122^\circ$ , with the formation of dibromo*isopilocarpine* (the lactone).

In the oxidation of pilocarpine by chromic acid, besides pilocarpoeic acid, a substance,  $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_2$ , is formed, which crystallises in small plates melting at  $153^\circ$ ; it probably does not contain the group which forms the lactone ring in pilocarpine.

Pilopie acid,  $\text{C}_7\text{H}_{10}\text{O}_4$ , obtained by Jowett in oxidising *isopilocarpine* with permanganate, does not appear to be the lactone of pilomalic acid,  $\text{C}_7\text{H}_{12}\text{O}_5$ , prepared by oxidising pilocarpoeic acid, as on heating pilomalic acid a dibasic acid is obtained, whilst pilopie acid is monobasic; again, ethyl pilomaleate yields an amide melting at  $190$ – $191^\circ$ , whereas Jowett's diamide melts at  $160^\circ$ .

K. J. P. O.

**Conversion of Tropidine into Tropine.** By ALBERT LADENBURG (*Ber.*, 1902, 35, 2295–2297).—Polemical, in reply to Willstätter (this vol., i, 559).

A. H.

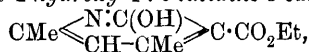
**Formation of 2-Pyrrolidinecarboxylic Acid by Alkaline Hydrolysis of Casein.** By EMIL FISCHER (*Zeit. physiol. Chem.*, 1902, 35, 227—229).—Casein is less readily hydrolysed by sodium hydroxide solution than by hydrochloric acid, but furnishes with the former a mixture of amino-acids from which, by the process already described (Abstr., 1901, i, 192), about 2.5 per cent. of crude 2-pyrrolidinecarboxylic acid in the lævo- and racemic forms was isolated (Abstr., 1901, i, 780). T. A. H.

**Condensation Products of Pyrrole.** By GIUSEPPE PLANCHER (*Ber.*, 1902, 35, 2606—2608).—The base,  $C_{12}H_{17}N$ , formed from 2:5-dimethylpyrrole by reduction with zinc dust and glacial acetic acid, yields a *hydriodide*,  $C_{12}H_{18}NI$ , which crystallises in colourless prisms melting above  $270^{\circ}$ . Probably the 2:5-dimethylpyrrole is first hydrolysed to acetylacetone, which, condensing with some of the unaltered compound, forms the base  $C_{12}H_{15}N$ , which finally undergoes reduction to  $C_{12}H_{17}N$ .

An intermediate compound,  $C_{12}H_{15}N$ , is obtained when 2:4-dimethylpyrrole is condensed with 90 per cent. acetic acid and zinc dust or zinc acetate; it crystallises in colourless needles and melts at  $74^{\circ}$ ; the *aurichloride* forms light yellow needles or prisms melting at  $109^{\circ}$  and the *platinichloride* orange-red prisms decomposing at  $213^{\circ}$ . It does not combine with methyl iodide in the cold, and although giving a faint pine wood coloration and the indole reaction with anhydrous oxalic acid, does not furnish the ordinary pyrrole indications with isatin and phenanthraquinone.

The views put forward as to the preceding condensations are confirmed by condensing pyrrole with acetylacetone, zinc acetate, and glacial acetic acid, when the base  $C_{10}H_{11}N$  is produced; this crystallises in colourless needles, melts at  $101$ — $102^{\circ}$ , gives the usual pyrrole colorations with isatin and pine wood, and develops a coloration with oxalic acid; it also yields a crystalline picrate. G. T. M.

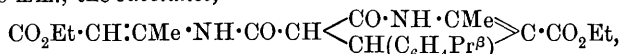
**Action of Malonic Ether and Malonamide on Aminoacetylacetone.** By EMIL KNOEVENAGEL and W. CREMER (*Ber.*, 1902, 35, 2390—2396).—*Ethyl 2-hydroxy-4:6-lutidine-3-carboxylate*,



prepared by condensing ethyl malonate with aminoacetylacetone in presence of sodium, crystallises from alcohol in long, slender needles, and from water in glistening tablets, melts at  $136^{\circ}$ , and does not react with nitrous acid or with hydroxylamine. The *hydrochloride* melts at  $95^{\circ}$ . The free acid,  $C_8H_9O_3N$ , formed as a bye-product, crystallises from alcohol, melts at  $254^{\circ}$ , and yields  $\psi$ -lutidostyryl when heated at  $260^{\circ}$ . The *amide*, prepared by condensing malonamide with aminoacetylacetone, crystallises from hot water with  $1H_2O$ , which it loses at  $110^{\circ}$ , melts at  $224^{\circ}$ , dissolves in hydrochloric acid and in aqueous sodium hydroxide, is hydrolysed when heated with strong potassium hydroxide, and yields  $\psi$ -lutidostyryl when boiled with 25 per cent. hydrochloric acid. T. M. L.

**Syntheses in the Pyridine Series. IV. An Extension of Hantzsch's Dihydropyridine Syntheses.** By EMIL KNOEVENAGEL and RICHARD BRUNSWIG (*Ber.*, 1902, 35, 2172—2184. Compare

Abstr., 1898, i, 447—449).—Attempts to condense ethyl cuminyldenemalonate and ethyl  $\beta$ -aminocrotonate in mol. proportion failed to give a definite product. On heating 1 mol. of the former, however, with 2 mols. of the latter for 12 hours at 140—155° in a vacuum of 30—50 mm., the *substance*,



is obtained; it separates from alcohol in small, white crystals, melts at about 166—168°, and when heated with 20 per cent. hydrochloric acid at 110—120°, or boiled with acetic anhydride containing sodium acetate, is hydrolysed to *ethyl 4-isopropylphenyldihydro-2-picolone-5-carboxylate*,  $\text{NH} \begin{array}{c} \text{CO} \text{---} \text{CH}_2 \\ \text{CMe} : \text{C}(\text{CO}_2\text{Et}) \end{array} \text{CH} \cdot \text{C}_6\text{H}_4\text{Pr}^\beta$ ; the latter is obtained from alcohol in white crystals and melts at 182—183°.

When ethyl 4-phenyldihydro-2-picolone-3:5-dicarboxylate (ethyl 6-oxy-4-phenyl-2-methyltetrahydropyridine-3:5-dicarboxylate) is rapidly hydrolysed by being dropped into a boiling 8 per cent. solution of sodium hydroxide, it gives *4-phenyldihydro-2-picolone-5-carboxylic acid*,  $\text{NH} \begin{array}{c} \text{CO} \text{---} \text{CH}_2 \\ \text{CMe} : \text{C}(\text{CO}_2\text{H}) \end{array} \text{CHPh}$ , which separates from alcohol in white crystals, melts and decomposes at 189—190°, and forms a white, anhydrous *silver* salt; on being heated with 20 per cent. hydrochloric acid for 8 hours at 100°, the acid is converted into  $\gamma$ -acetyl- $\beta$ -phenylbutyric acid, and by simple melting is transformed, with loss of carbon dioxide, into *4-phenyldihydro-2-picolone*,  $\text{NH} \begin{array}{c} \text{CO} \text{---} \text{CH}_2 \\ \text{CMe} : \text{CH} \end{array} \text{CHPh}$ , which crystallises from chloroform or dilute acetic acid and melts and decomposes at 271—273°.

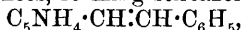
If in heating ethyl cuminyldenemalonate with ethyl  $\beta$ -aminocrotonate in a vacuum the temperature rises above 160°, considerable quantities of ethyl 5:7:4-trihydroxy-2-methylquinoline-6-carboxylate are formed (compare Knoevenagel and Fries, Abstr., 1898, i, 448).

Ethylethyldenemalonate (1 mol.), and ethyl  $\beta$ -aminocrotonate (1 mol.), readily combine at the ordinary temperature to form *ethyl dihydro-2-lutidone-3:5-dicarboxylate* (*ethyl 2-oxy-4:6-dimethyltetrahydropyridine-3:5-dicarboxylate*),  $\text{NH} \begin{array}{c} \text{CO} \cdot \text{CH}(\text{CO}_2\text{Et}) \\ \text{CMe} : \text{C}(\text{CO}_2\text{Et}) \end{array} \text{CHMe}$ , which crystallises from ether, melts at 54—54·5°, and is converted by 20 per cent. hydrochloric acid at 110—115° into  $\beta$ -methyl- $\delta$ -pentanone- $\alpha\alpha$ -dicarboxylic acid,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH}(\text{CO}_2\text{H})_2$ ; this is a colourless oil, easily soluble in water, which yields a stable *silver* salt, a *diethyl* salt boiling at 150—170° under 15 mm. pressure, and loses carbon dioxide when heated at 120°, giving  $\gamma$ -acetyl- $\beta$ -methylbutyric acid. The latter boils at 153—154° under 11 mm. pressure (von Schilling, *Diss.*, Halle, 1899, gives 141° under 15 mm. pressure), and forms an *ethyl* salt boiling at 110—111° under 13 mm. pressure.

On heating ethyl ethyldenemalonate with ethyl  $\beta$ -aminocrotonate for 6 hours at 120—140° in a vacuum, the principal product is the *ester*,  $\text{CO}_2\text{Et} \cdot \text{CH} : \text{CMe} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH} \begin{array}{c} \text{CO} \text{---} \text{NH} \\ \text{CHMe} : \text{C}(\text{CO}_2\text{Et}) \end{array} \text{CMe}$ ; it

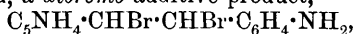
crystallises from alcohol, melts at 155—157°, and is hydrolysed by 20 per cent. hydrochloric acid at 100° to a substance melting at 196—197° (probably *ethyl 4-methyldihydro-2-picolone-5-carboxylate*). W. A. D.

Some Derivatives of 2-Picoline (Nitro- and Amino-stilbazoles). By KARL FEIST (*Arch. Pharm.*, 1902, 240, 244—257).—Unlike chloral (Einhorn, Abstr., 1892, 75), acetaldehyde and benzaldehyde do not condense with  $\alpha$ -picoline when heated with this substance and some amyl acetate even at 160°. The former does not even react in the presence of zinc chloride at 200°; benzaldehyde, however, does react in these circumstances, forming stilbazole,



(Baurath, Abstr., 1888, 65, 608). Bromal and butylchloral do not react with  $\alpha$ -picoline.

The nitrobenzaldehydes, like benzaldehyde, condense with  $\alpha$ -picoline to form nitrostilbazoles,  $\text{C}_5\text{NH}_4\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$  (Abstr., 1901, i, 290). These are reduced by zinc and hydrochloric acid to oily *aminostilbazoles*,  $\text{C}_5\text{NH}_4\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ . The last substances are di-acid bases, but their hydrochlorides (which melt at 250—254°, 240°, and 260° in the case of the ortho-, meta- (with  $2\text{H}_2\text{O}$ ), and para-isomerides respectively) lose hydrogen chloride at 100°; in the case of the meta-compound, a *dibromo-additive product*,



was prepared, and with hydrochloric acid this forms only a mono-hydrochloride melting at 86—96°, which is partly decomposed by water. C. F. B.

**4-Hydroxyisocarbostryl. II.** By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1902, 35, 2421—2430. Compare Abstr., 1900, i, 359).—4-Hydroxyisocarbostryl is best obtained from methyl 4-hydroxyisocarbostrylcarboxylate (prepared from ethyl phthalylaminoacetate), by boiling it with dilute sulphuric acid (compare *loc. cit.*).

4-Methoxyisocarbostryl,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO} \\ \diagup \\ \text{C(OMe)} \end{smallmatrix} \begin{smallmatrix} \text{NH} \\ \diagdown \\ \text{CH} \end{smallmatrix}$ , is prepared from hydroxyisocarbostryl by heating with sodium methoxide and methyl iodide at 100°; it crystallises in needles melting at 171° and, when boiled with phosphorus oxychloride, is converted into chloromethoxyisquinoline (m. p. 77°).

By the action of fuming nitric acid, hydroxyisocarbostryl is converted into phthaloneimide (m. p. 224°).

The *phthalide* of hydroxyisocarbostryl is formed on heating the latter with phthalic anhydride at 240°; it crystallises in flattened, orange needles melting at 314°, and is decomposed into its constituents by warming with concentrated potassium hydroxide; by cautious treatment with alkalis, it yields *hydroxyisocarbostrylphthaloylic acid*,

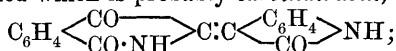
$\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H} \\ \diagup \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$ , forming pale yellow leaflets which

do not melt at 265°. On heating hydroxyisocarbostryl and benzaldehyde in the presence of a trace of piperidine, a *benzylidene* derivative,

$\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \diagup \\ \text{CO}\cdot\text{C} \end{smallmatrix} \begin{smallmatrix} \text{CHPh} \\ \diagdown \end{smallmatrix}$ , is formed which exists in two forms, one crystal-

lising in small, soluble, yellow prisms melting at 193—194°, the other crystallising in lemon-yellow needles melting at 165°, and when heated at 170° changing into the other form.

When hydroxyisocarbostyryl is heated with isatin at 210°, a substance is formed which is probably *carbindirubin*,



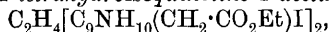
it crystallises in reddish-brown needles melting at 297—299°.

On cautiously oxidising hydroxyisocarbostyryl in solution in hydrochloric acid with potassium dichromate, dihydrocarbindigo is obtained as orange-yellow, microscopic needles, identical with the product of the reduction of carbindigo. Carbindigo is best prepared by oxidising hydroxyisocarbostyryl with hydrogen peroxide, and is also formed when the latter is heated at 210° with phthaloneimide; when its alkaline solution is boiled with free access of air, it is oxidised, ammonia and phthalic acid being formed; on reduction with hydriodic acid and red phosphorus, a little soluble substance,  $\text{C}_{18}\text{H}_{12}\text{O}_3\text{N}_2$ , is obtained, which crystallises in yellowish needles darkening at 300° and melting at 390—395°.

Molecular weight determinations of carbindigo in boiling nitrobenzene confirm the dimolecular formula,  $\text{C}_{18}\text{H}_{10}\text{O}_4\text{N}_2$ , previously ascribed to it (*loc. cit.*).  
K. J. P. O.

**A New Mode of Isomerism of Asymmetric Nitrogen.** By EDGAR WEDEKIND (*Compt. rend.*, 1902, 134, 1356—1359).—Compounds containing two asymmetric carbon atoms seem to be capable of existing in stereoisomeric forms differing in chemical properties and produced by different reactions.

*Ethyl ethylenebis-1-tetrahydroisoquinoline-1-acetate di-iodide*,



exists in two isomeric forms according as to whether it is produced from ethyl tetrahydroisoquinolyl acetate,  $\text{C}_9\text{NH}_{10} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , and ethylene di-iodide, or from ethyl iodoacetate and *ethylenebistetrahydroisoquinoline*,  $\text{C}_2\text{H}_4(\text{C}_9\text{NH}_{10})_2$ .

The isomeride obtained by the first process is the more stable; it is produced by heating its generators until a homogeneous mixture is formed and allowing the product to solidify. When crystallised from alcohol, it separates in plates melting at 168—169°.

The labile isomeride formed by heating ethylenebistetrahydroisoquinoline with excess of ethyl iodoacetate at 50° is obtained as a yellow, pulverulent substance decomposing at 52° with the evolution of ethyl iodoacetate. This decomposition also takes place either on allowing the di-iodide to remain for some time at the ordinary temperature or by warming it with water; under these conditions, a monoiodide,  $\text{C}_9\text{NH}_{10} \cdot \text{C}_2\text{H}_4 \cdot \text{C}_9\text{NH}_{10} \cdot \text{I} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , is produced, this salt melting at 158°.

The ethylenebistetrahydroisoquinoline required for this preparation is obtained by mixing together ethylene dibromide and tetrahydroisoquinoline in the theoretical proportion. After 12 hours, the mixture is treated with ether in the presence of alcohol and sodium carbonate;

the base is isolated on evaporating off the solvent and crystallised from petroleum. It forms almost colourless crystals and melts at 98°.

G. T. M.

**Action of Alkalis on Phenanthridine and Acridine Methiodides.** By AMÉ PICTET and E. PATRY (*Ber.*, 1902, **35**, 2534—2537).—The methiodides of phenanthridine and acridine, when treated with alkalis, behave in a similar manner to quinoline and pyridine methiodides (see Decker, *Abstr.*, 1892, 879). Phenanthridine methiodide, when treated with sodium hydroxide, yields phenanthridine methohydroxide (see *Abstr.*, 1891, 837), which, when distilled with steam, gives the volatile 10-methyl dihydrophenanthridine (Ankersmit, *Dissertation*, Bern, 1891) and leaves 10-methylphenanthridone (*Abstr.*, 1893, i, 658).

Acridine methiodide yields analogous products. *N*-Methyl dihydroacridine separates from water in compact crystals, melts at 96°, is volatile with steam, and is oxidised in air to 10-methylacridone.

R. H. P.

**Isomeride of Quinophthalone.** By ALEXANDER EIBNER and H. MERKEL (*Ber.*, 1902, **35**, 2297—2301. Compare *Abstr.*, 1901, i, 611).—An isomeride of quinophthalone is produced when phthalic anhydride is heated with quinaldine at 100—160°, the yield varying from 10—20 per cent., according to the temperature; this compound crystallises in monoclinic, orange-yellow tablets and melts at 186°. It is converted into quinophthalone by being heated with benzaldehyde, or heated alone at 240—250° for three hours; when heated at 100° with fuming sulphuric acid, it yields the same derivative as quinophthalone. In its reactions, it differs considerably from the isomeric compound. Alcoholic ammonia, which converts quinophthalone into  $\alpha$ -quinophthaline, decomposes the new isomeride, yielding quinaldine and phthalamide. Aniline yields quinaldine and phthalanil. Phenylhydrazine yields phthalylphenylhydrazine and quinaldine. Hydroxylamine also yields quinaldine together with a small amount of a red substance which is probably a hydroxylamine derivative of quinaldine. Bromine converts the new isomeride into a dibromo-derivative,  $C_{18}H_{11}O_2NBr_2$ , which crystallises in silky needles melting indefinitely at about 200°; this substance is reconverted into the original compound when boiled with ammonia or aqueous soda, whilst aniline converts it into phthalanil. A. H.

**Action of Ethyl  $\beta$ -Chloroacetoacetate on Diazo-chlorides.** By G. FAVREL (*Compt. rend.*, 1892, **134**, 1312—1313).—By the action of ethyl  $\beta$ -chloroacetoacetate on an aqueous solution of diazobenzene chloride, yellowish, voluminous crystals are obtained of *ethyl chloroglyoxylate phenylhydrazone*,  $NHPh \cdot N : CCl \cdot CO_2Et$ , which melts at 80—81°. Using diazo-*p*-toluene chloride, *ethyl chloro-oxalate-p-tolyl hydrazone* is obtained which melts at 103—104°; the corresponding *o-tolylhydrazone* melts at 74—75°.

The action is similar to that of ethyl methylacetoacetate and ethyl ethylacetoacetate studied by Japp and Klingemann (*Proc.*, 1887, **3**, 142).

J. McC.

**Action of Phenylhydrazine and of Phenylmethylhydrazine on  $\alpha$ - $\beta$ -Dichloro- $p$ -methylstyrene.** By FRANZ KUNCKELL and FRANZ VOSSEN (*Ber.*, 1902, 35, 2291—2294).—Phenylhydrazine reacts with  $\alpha$ - $\beta$ -dichloro- $p$ -methylstyrene at the temperature of boiling water; the chlorine atoms are replaced by the phenylhydrazine residues, and then oxidation occurs at the expense of the excess of hydrazine, so that the final product is Müller and Pechmann's  $p$ -tolylglyoxalosazone (Abstr., 1890, i, 51), the hydrochloride of which melts at 155°.  $\alpha$ -Phenylmethylhydrazine reacts in a similar manner, yielding  $p$ -tolylglyoxal-dimethylphenylhydrazone,  $C_6H_4Me \cdot C(N \cdot NMePh) \cdot CH \cdot N \cdot NMePh$ , which crystallises in yellowish needles melting at 208° and readily soluble in benzene or alcohol. J. J. S.

**Action of Phenylhydrazine on  $\alpha\delta$ -Diketones.** By ALEXANDER SMITH and HERBERT N. MCCOY (*Ber.*, 1902, 35, 2169—2171).—Purified acetonylacetonebisphenylhydrazone, contrary to previous statements, can be exposed to the air for eighteen months without resinifying. *Bimolecular acetonylacetone monophenylhydrazone*,  $(C_{12}H_{14}N_2)_2$ , is obtained on adding hydrochloric acid to an alcoholic solution of equal weights of phenylhydrazine and acetonylacetone, or mol. proportions of acetonylacetone and its diphenylhydrazone; it crystallises from alcohol in colourless prisms, melts at 175.5°, and by cold concentrated hydrochloric acid is converted into an isomeric substance which is much less soluble in alcohol, forms rectangular plates, and melts at 188°.

Desyl- $\beta$ -acetonaphthone (Abstr., 1900, i, 38) interacts with phenylhydrazine dissolved in hot glacial acetic acid to form the pyridazine,  $CPh \begin{smallmatrix} \text{CPh}-CH \\ \text{NH} \cdot NPh \end{smallmatrix} C \cdot C_{10}H_7$ , which crystallises in bright yellow needles and melts at 192°.

Desyl- $\alpha$ -acetonaphthone, under the same conditions, is not affected.

W. A. D.

**2:6-Dibromo- $p$ -phenylenedi-imine.** By C. LORING JACKSON and DANIEL F. CALHANE (*Ber.*, 1902, 35, 2495—2496).—Dibromo- $p$ -phenylenediamine is converted by bromine into a green salt, which yields with alkalis a brownish-red base. This salt, which is decomposed both by water and alcohol, appears to be 2:6-dibromo- $p$ -phenylenedi-imine hydrobromide,  $C_6H_2Br_2(NH)_2 \cdot HBr$ .  $p$ -Phenylenediamine undergoes a similar reaction with bromine, a  $p$ -phenylenedi-imine hydrobromide being formed as a dark blue salt which yields a brownish-red base free from bromine.  $o$ -Phenylenediamine yields even less stable compounds than the para-derivative, whilst the  $m$ -compound reacts differently.

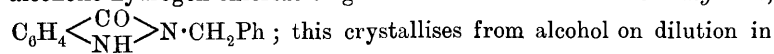
$p$ -Phenylenedi-imine appears to have been obtained by Heucke (*Annalen*, 1889, 255, 193), who, however, ascribed to it a higher molecular weight. A. H.

**Some New Indazole Derivatives.** By EMIL FISCHER and RICHARD BLOCHMANN (*Ber.*, 1902, 35, 2315—2319).—*Benzylidene- $o$ -hydrazinobenzoic acid*,  $CO_2H \cdot C_6H_4 \cdot NH \cdot N \cdot CHPh$ , obtained by adding benzaldehyde to an aqueous solution of  $o$ -hydrazinobenzoic acid at 50°, crystallises from ether in small, sulphur-yellow needles, sinters at

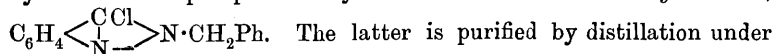
219°, and melts at 227—228° (corr.). When reduced with sodium amalgam, it gives *β*-benzyl-o-hydrazinobenzoic acid,



which crystallises from alcohol, on diluting with water, in slender needles, melts and decomposes at 134° (corr.), and is converted by warm alcoholic hydrogen chloride or glacial acetic acid into the *anhydride*,



this crystallises from alcohol on dilution in nearly colourless needles, melts at 180·5° (corr.), and is converted by an excess of phosphorus oxychloride into 3-chloro-2-benzylindazole,



The latter is purified by distillation under 0·25 mm. pressure, when it boils at about 132—134° (corr.); it then crystallises from light petroleum in small, colourless prisms melting at 47·5° (corr.). 2-Benzylindazole,  $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CH} \\ | \\ \text{N} \end{array} \right\rangle \text{N} \cdot \text{CH}_2\text{Ph}$ , obtained by

reduction with zinc dust and hydrochloric acid, crystallises from light petroleum in well-formed prisms and melts at 73° (corr.). The *picrate* W. A. D. melts at 167° (corr.).

**Some Salts of Antipyrine.** By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1902, [iii], 27, 612—615).—Antipyrine *hydrochloride*, obtained by concentrating on the water-bath a solution of antipyrine in concentrated aqueous hydrochloric acid with addition of alcohol, forms thick, tabular crystals melting at 158—160°; it is very deliquescent, very soluble in water, less so in absolute alcohol, very sparingly so in ether or benzene. The salt is hydrolysed in aqueous solution, and the amount dissolved can be readily estimated by titration with alkali, using phenolphthalein as indicator.

Antipyrine hydrochloride, although almost insoluble in benzene, is fairly soluble in a boiling mixture of benzene and absolute alcohol. From this solution, it crystallises in flat, elongated prisms which contain 1 mol. of benzene of crystallisation. It is very soluble in water with liberation of benzene.

If a benzene solution containing mol. proportions of antipyrine and *d*-camphorsulphonic acid is evaporated and kept in the cold, crystals of *antipyrine d-camphorsulphonate* are obtained; it is not deliquescent, but is very soluble in water with strongly acid reaction. The salt is best recrystallised from a mixture of acetone and absolute alcohol.

A. F.

**Isatin.** By A. KORCZYNSKI and LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1902, 245—260. Compare Abstr., 1901, 347, 415, 416, 615).—*a*-2- (or 3)-Chloroindophenazine,  $\text{C}_6\text{H}_4 \cdot \text{C} : \text{N} : \text{C} : \text{CH} : \text{CH}$   
 $\text{NH} - \text{C} : \text{N} : \text{C} : \text{CH} : \text{CCl}$ , formed

by boiling *p*-chloro-*o*-phenylenediamine with isatin in acetic acid solution, crystallises from alcohol in light yellow needles or scales, is easily soluble in acetone or chloroform, and melts above 300°. On addition of ammoniacal silver nitrate solution, the alcoholic solution yields a red precipitate. On boiling with glacial acetic acid, an *acetyl*



derivative is formed, which is easily soluble in acetone, benzene, ether, or chloroform, moderately so in alcohol, from which it crystallises in white needles melting at 208°. By condensation of acetylisisatin with chloro-*o*-phenylenediamine hydrochloride in hot acetic acid solution in presence of sodium acetate,  $\beta$ -2- (or 3)-chloroindophenazine and two isomeric chlorohydroxyacetylaminophenylquinoxalines are formed.

$\beta$ -2- (or 3)-*Chloroindophenazine* is soluble with difficulty in acetic acid, very slightly in alcohol or ether, crystallises in yellowish needles, and melts at 310°.  $\beta$ -6- (or 7)-*Chloro-3-hydroxy-2-o-aminophenylquinoxaline*,  $\text{OH}\cdot\text{C}_8\text{N}_2\text{H}_3\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , easily soluble in alcohol or acetone, less so in benzene, chloroform, or ether, crystallises in orange-coloured needles and melts at 229—230°, gives a red colour on addition of ether to its solution in concentrated hydrochloric acid, and when boiled with glacial acetic acid gives  $\beta$ -2- (or 3)-chloroindophenazine.

$\alpha$ -6- (or 7)-*chloro-3-hydroxy-2-o-aminophenylquinoxaline*, which is less soluble in organic solvents than the  $\beta$ -modification, forms yellowish-brown scales, melts at 265°, gives a red colour on addition of ether to the solution in concentrated hydrochloric acid, forms a white hydrochloride, and on boiling with glacial acetic acid yields  $\alpha$ -2- (or 3)-chloroindophenazine.

9-*Bromoindophenazine*, formed by condensation of acetylbromoisatin with *o*-phenylenediamine, is sparingly soluble in alcohol, ether, acetone, benzene, or chloroform, forms yellow needles, melts at 279—280°, and yields a red precipitate on addition of ammoniacal silver nitrate to its alcoholic solution.

3-*Hydroxy-2-m-bromo-o-aminophenylquinoxaline*, formed together with bromoindophenazine, is easily soluble in aqueous alkalis, ether, or acetone, sparingly in alcohol, benzene, or chloroform, forms orange-coloured needles and melts at 249—250°. It yields a red colour on addition of ether to its solution in concentrated hydrochloric acid. With concentrated sodium hydroxide solution, it forms a white precipitate, probably the *sodium* derivative. The *picryl* derivative,  $\text{C}_{14}\text{H}_9\text{ON}_3\text{Br}\cdot\text{C}_6\text{H}_2\text{O}_6\text{N}_3$ , formed by boiling the quinoxaline with picryl chloride in alcoholic solution, is easily soluble in aqueous alkalis or acetone, sparingly in alcohol, ether, benzene, or chloroform, crystallises from acetic acid in red needles and melts at 287—288°.

3-*Hydroxy-2-m-bromo-o-aminophenyl-6- (or 7)-methylquinoxaline*, obtained from acetylbromoisatin and *o*-tolylenediamine, forms yellow-orange coloured needles and melts at 243°.

6- (or 7)-*Chloro-3-hydroxy-2-o-hydroxyphenylquinoxaline*, obtained by boiling *o*-chlorophenylenediamine with *o*-hydroxybenzoylformic acid in aqueous solution, dissolves easily in alkalis, concentrated acids, or boiling alcohol, sparingly in benzene, ether, or chloroform, crystallises in yellow needles, and melts at 286—287°. It forms a dark reddish-brown solution in sulphuric acid which, on heating, becomes yellow with formation of the *sulphonic* acid, the *sodium* salt of which crystallises with  $3\text{H}_2\text{O}$ . On distillation of the *barium* sulphonate, which crystallises in minute, yellowish-white needles, 2- (or 3)-*chlorocumaro-*

*phenazine*,  $\begin{array}{c} \text{C}_6\text{H}_4\cdot\text{C}:\text{N} \\ \text{O}=\text{C}:\text{N} \end{array} > \text{C}_6\text{H}_3\text{Cl}$ , is obtained, which crystallises in

white needles, is easily soluble in alcohol, benzene, or chloroform, and melts at 149—150°. Its solutions have a faintly green fluorescence.

5-Tolyl- $\psi$ -indophenazine,  $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \\ \parallel \quad \nearrow \\ \text{N} = \text{C} \cdot \text{N}(\text{C}_7\text{H}_7) \end{array} > \text{C}_6\text{H}_4$ , obtained from

isatin and *o*-amino-*p*-methyl-diphenylamine, is easily soluble in boiling alcohol, less so in benzene or chloroform; in concentrated acids, it forms yellow or reddish-brown solutions, crystallises in glistening, brownish-red needles, and melts at 255—255.5°. The hydrochloride, formed by passing hydrogen chloride through its solution in benzene, is a yellow, crystalline powder which gives off hydrogen chloride when dry. 9-Bromo-5-tolyl- $\psi$ -indophenazine, obtained by using bromoisatin, dissolves in acids with a yellow coloration, easily in boiling alcohol, less readily in benzene, chloroform, or acetone, with difficulty in ether, crystallises in brownish-red needles, and melts at 290—291°.

The benzyl ether of isatinoxime, whether obtained by the action of benzyl chloride on the silver salt of isatinoxime or by the condensation of isatin with  $\alpha$ -benzylhydroxylamine, dissolves easily in alcohol, acetone, benzene, or ether, sparingly in alkalis, crystallises in yellow needles, and melts at 168.5—169°. The alcoholic solution yields a red precipitate on addition of ammoniacal silver nitrate. The ethers of isatinoxime made from the silver salt have therefore the grouping C·O·R. Bromoisatinoxime benzyl ether, made from bromoisatin and  $\alpha$ -benzylhydroxylamine, forms yellow needles easily soluble in boiling alcohol, acetone, benzene, or chloroform, and melts at 200°.

Chloroisatinoxime benzyl ether forms yellow needles soluble with difficulty in alcohol or ether, more easily in benzene or chloroform, and melts at 224.5°.

Nitroisatinoxime benzyl ether forms golden-yellow scales soluble with difficulty in alcohol, more easily in acetone or benzene, and melts at 234—235°.

The spectra of isatin, chloroisatin, and methylisatin show a well-defined absorption band in the region of K $\beta$  and a strong end absorption. Nitroisatin and acetylisatin show no characteristic band; this may be due to their existence in solution as isatic acids, as sodium isatate shows a similar spectrum and both nitro- and acetyl-isatin easily form quinoxalines. Indophenazine and chloroindophenazine show no characteristic absorption bands, but 5-tolyl- $\psi$ -indophenazine and 5-methyl- $\psi$ -indophenazine show two very distinct bands beyond the thallium line.

G. Y.

**Intramolecular Rearrangement of Atoms in Azoxybenzene and its Derivatives.** By H. M. KNIPSCHER (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 5, 51—53. Compare *Ber.*, 1885, 18, 1405).—The isomeric change of azoxybenzene and its derivatives into hydroxyazobenzenes, takes place with formation of the *para*- and *ortho*-isomerides on heating at 200°, with formation of the *ortho*-isomeride only on exposure to direct sunlight or, in the case of azoxybenzene, on heating with acetic anhydride at 200°.

The action of acetyl chloride on azoxybenzene leads to the formation of di-*p*-chloroazobenzene and *p*-chloroacetanilide; of benzoyl chloride

and of phosphorus pentachloride, to the formation of azobenzene, in the latter case with evolution of chlorine; and of aluminium chloride to the formation of *p*-chloroazobenzene.

The isomeric change was not brought about by the action of butyryl chloride, phosphorus oxychloride, phosphoric acid, aqueous sodium hydroxide, copper oxide, zinc oxide, or zinc carbonate.

Azoxybenzene purified by heating with Beckmann's mixture at 150—180°, is perfectly white. G. Y.

**Azoxybenzylidene Bases.** By FRIEDRICH J. ALWAY (*Ber.*, 1902, 35, 2434—2438).—*p*-Azoxybenzylideneaniline,  $\text{ON}_2(\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NPh})_2$ , can be prepared from *p*-azoxybenzaldehyde and aniline, or by adding solid sodium hydroxide to a boiling alcoholic solution of *p*-nitrobenzyl-aniline, or by boiling benzyl chloride (1 mol.) with aniline (6 mols.), adding alcohol and then sodium hydroxide; the yield represents 75 per cent. of the theoretical; this substance crystallises in golden-yellow leaflets, melting at 185°.

*p*-Azoxybenzylidene-*o*-toluidine,  $\text{ON}_2(\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_7\text{H}_7)_2$ , prepared in a similar manner, crystallises in lustrous orange leaflets melting at 182—183°; the *m*-toluidine derivative melts at 133°, and the *p*-toluidine derivative at 188—190°.

*p*-Azoxybenzaldehyde is formed when the above compounds are suspended in dilute nitric acid, and crystallises in long, yellow needles melting at 194—195.5° (corr.); it dissolves in sulphuric acid with an orange coloration, and on heating the solution at 120° is converted into hydroxyazo-dyes. This compound is identical with the substance (m. p. 190°), obtained by Gattermann by the electrolytic reduction of *p*-nitrobenzaldehyde (*Abstr.*, 1897, i, 188), and with that prepared by Kirpal (m. p. 194°, *Abstr.*, 1897, i, 520). K. J. P. O.

**Azo-compounds of Acetylacetone.** By CARL BÜLOW and FRITZ SCHLOTTERBECK (*Ber.*, 1902, 35, 2187—2191).—*o*-, *m*-, and *p*-Nitrodiazobenzene will condense with acetylacetone, not only in alkaline or neutral solution, but also in a strongly acid solution. The azo-derivatives thus formed cannot be converted into acetylated hydrazones, as can other phenylazo-derivatives of acetylacetone.

Phenylazoacetylacetone is easily prepared by mixing solutions of benzenediazonium chloride, acetylacetone, and sodium acetate (compare Beyer and Claisen, *Abstr.*, 1888, 827); it crystallises in long, yellow needles melting at 90°, and when boiled with aqueous sodium hydroxide, is converted into aniline and a substance,  $\text{C}_{15}\text{H}_{16}\text{O}_4$ , which crystallises in white needles melting at 186°.

1-Phenyl-3 : 5-dimethyl-4-benzeneazopyrazole was obtained by boiling an acetic acid solution of mol. proportions of phenylhydrazine and acetylacetone (compare Beyer and Claisen, *loc. cit.*); it melts at 62°.

*p*-Nitrophenylazoacetylacetone,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{CH}(\text{COMe})_2$ , is prepared by mixing alkaline solutions of acetylacetone and *p*-nitroisodiazobenzene, or acid solutions of acetylacetone and *p*-nitrobenzenediazonium chloride; it crystallises in brownish-yellow needles, melting

at 221—222°; the corresponding *o*-nitro-derivative forms yellowish-red needles melting at 180°, and the *m*-nitro-derivative orange-yellow leaflets melting at 140°.

K. J. P. O

**Benzene-*p*-azobenzaldehyde.** By PAUL FREUNDLER (*Compt. rend.*, 1902, 134, 1359—1361).—The reduction of a mixture of nitrobenzene and *p*-nitrobenzaldehyde, in molecular proportion, by an alcoholic solution of sodium hydroxide and zinc dust, leads to the production of a mixture of hydrazo-derivatives, which, when subsequently oxidised by yellow mercuric oxide, give rise to azobenzene and the *methyl ethers* of benzene-*p*-azobenzaldehyde and *s.p*-azodibenzaldehyde. The symmetrical diacetal,  $N_2[C_6H_4 \cdot C(OMe)_2]_2$ , is separated from the other products by its sparing solubility in alcohol; it crystallises from this solvent or ether in orange-coloured flakes and melts at 118°.

*s.p*-Azodibenzaldehyde,  $N_2(C_6H_4 \cdot COH)_2$ , obtained by hydrolysing its methyl acetal with dilute sulphuric acid, crystallises in reddish-brown flakes from amyl alcohol or nitrobenzene, but is almost insoluble in the other organic solvents. Its *diphenylhydrazone* crystallises from nitrobenzene in dark red needles melting and decomposing at 278.5°; it dissolves in concentrated sulphuric acid to a deep blue solution.

Benzene-*p*-azobenzaldehyde, prepared by hydrolysing its acetal derivative, crystallises from acetone in red leaflets and melts at 120°; it is soluble in the ordinary organic solvents, excepting light petroleum; its *phenylhydrazone* crystallises from alcohol in red needles and melts at 165—166°.

The two aldehydes may be readily sublimed without decomposition.

G. T. M.

**Di-*p*-nitrohydrazobenzene.** By PAUL FREUNDLER and L. BÉRANGER (*Compt. rend.*, 1902, 134, 1219—1221).—When the di-*p*-nitroazobenzene, melting at 220° and obtained by the action of nitric acid on diacetylhydrazobenzene, is reduced with ammonium sulphide, it yields a crystalline, orange-yellow compound which melts and decomposes at about 280° and agrees in its composition and properties with the di-*p*-nitrohydrazobenzene obtained by Willgerodt, Werner, and Rassow by reducing di-*p*-nitroazobenzene, except that its melting point is higher. No trace of this product can, however, be obtained by the hydrolysis of the dinitrodiacetylhydrazobenzene, which is the principal product of the nitration of diacetylhydrazobenzene. It would seem, therefore, that the yellow compound is not a true dinitrohydrazobenzene, but a tautomeric modification of it,  $N_2(C_6H_4 \cdot NO \cdot OH)_2$ . The molecular compound of azobenzenediacylhydrazobenzene previously described, yields, on nitration, only a mixture of dinitroazobenzene and dinitrodiacetylhydrazobenzene.

C. H. B.

**Oxime of *o*-Azidobenzaldehyde [*o*-Triazobenzaldehyde].** By EUGEN BAMBERGER and ED. DEMUTH (*Ber.*, 1902, 35, 1885—1896. Compare Abstr., 1901, i, 392, 621).—When *o*-triazobenzaldoxime is dissolved in aqueous sodium hydroxide and the solution boiled for some time, the following compounds are produced: (1), a crystalline acid,  $C_7H_6ON_2$ ; (2), an amorphous acid,  $C_7H_6ON_2$ ; (3), a neutral substance,  $C_7H_6ON_4$ ; (4), *o*-aminobenzaldoxime; (5), *o*-triazobenzoic acid,

$N_3 \cdot C_6H_4 \cdot CO_2H$ ; (6), anthranilic acid (?); (7), small quantities of unidentified substances.

The neutral substance,  $C_7H_6ON_4$ , isomeric with *o*-triazobenzaldoxime, is shown to be *o*-triazobenzamide,  $N_3 \cdot C_6H_4 \cdot CO \cdot NH_2$ , and its formation is of interest as showing that the Beckmann type of isomeric change may take place under the influence of alkalis; it crystallises from dilute sodium hydroxide in long, colourless, silky needles, melts at  $135.5$ — $136^\circ$ , and can be synthesised from *o*-triazobenzoic acid by the action of phosphorus pentachloride and then of ammonia.

The crystalline acid,  $C_7H_6ON_2$ , is shown to be 2-hydroxyindazole,  $C_6H_4 \left\langle \begin{smallmatrix} CH \\ N \end{smallmatrix} \right\rangle N \cdot OH$ , and its formation is analogous to that of anthranil,

formulated as  $C_6H_4 \left\langle \begin{smallmatrix} CH \\ N \end{smallmatrix} \right\rangle O$ , from *o*-triazobenzaldehyde (Abstr., 1901, 95 and 127); it may be regarded as the oxime of anthranil; it crystallises from water in white needles, and from ether in glistening prisms, melts at  $139$ — $139.5^\circ$ , and dissolves in alkali carbonates and hydrogen carbonates. The acid *silver* salt,  $C_7H_5ON_2Ag, C_7H_6ON_2$ , forms a white, crystalline precipitate, detonates when heated, becomes brown at  $190^\circ$ , sinters, and then melts and decomposes at  $202.5$ — $203.5^\circ$ .

Nitroso-2-hydroxyindazole,  $NO \cdot C_6H_3 \left\langle \begin{smallmatrix} CH \\ N \end{smallmatrix} \right\rangle N \cdot OH$ , crystallises from water in red, silky needles, dissolves readily in alcohol or acetone and in alkalis, hydroxides, and ammonia, sinters at  $156^\circ$ , becomes dark and explodes at  $167^\circ$ , and gives Liebermann's reaction. Hydroxyindazole is reduced by tin and hydrochloric acid or by zinc dust and ammonium chloride to E. Fischer's indazole.

The amorphous acid,  $C_7H_6ON_2$ , is possibly a polymerised hydroxy-indazole.

T. M. L.

**The Properties of Proteids of combining with Acids.** By LADISLAUS VON RHORER (*Pflüger's Archiv*, 1902, 90, 368—388).—In the estimation of equivalent quantities of proteid and acid the precipitation method is the best. The results obtained are independent of the nature of the precipitant and of excess of acid. The fact that proteids are precipitable by alkaloid reagents from acid solutions only, is due to slight dissociation, and therefore depends on the basic character of proteids. Proteids are amphoteric electrolytes.

W. D. H.

**The Chemical Action between Proteids and Aniline Dyes.** By MARTIN HEIDENHAIN (*Pflüger's Archiv*, 1902, 90, 115—230).—The reaction between proteids and aniline dyes is regarded as more of a chemical than of a simply physical nature. Proteids can react with both bases and acids, and can thus combine with both acidic and basic dyes. As a rule, with a special proteid either the acidic or basic character is the more pronounced, and there is thus a greater tendency to form compounds with basic or acidic dyes.

The action of aromatic sulphonic acids on proteids is largely a function of the relative acidity of the acid. The greater the strength

of the acid, the more readily are the proteids precipitated. The precipitation is probably accompanied by a conversion of the proteids into acid albumins.

Although a number of neutral dye salts do not precipitate proteids, yet the free acids or bases corresponding with these salts readily form coloured precipitates. For example, egg-albumin is not precipitated by naphthol yellow S, or by indigocarmin, and yet is readily precipitated by these reagents in the presence of a little acetic acid.

The action of some 30 acidic dyes on albumin and casein under varying conditions has been studied, and the results tabulated. Feebly acidic dyes are the best reagents for the precipitation, stronger acids are not so active, owing probably to their high molecular weights. Violet black is capable of precipitating extremely dilute solutions of proteids in the presence of acetic acid. The presence of amino-groups in an acid dye tends, in most cases, to lessen the precipitating power of the dye. The most active precipitating agents are ponceau 2R and 3R, palatine-red and new coccin.

Acetic acid is capable of changing the colour of congo-red to blue, but in the presence of small amounts of serum-albumin the change in colour does not occur. Aminoazosulphonic acids combine with proteids even in the presence of a large excess of acetic acid, and certain of the products formed dissolve in glacial acetic acid without undergoing decomposition. The colours of the proteid compounds resemble those of the sodium salts of the dye. Varying amounts of dye are taken up by the proteid, and the colour of the product becomes darker as the amount of dye increases. When only minute quantities of the acid dye are employed, the compound remains in solution, but a slight increase in the amount of dye precipitates the proteid in the form of a coloured albumin sulphonate.

Anthracene-blue and alizarin-brown are capable of precipitating certain proteids. In some cases, the amount of mineral matter present in the proteid affects the precipitation.

Basic dyes are also capable of precipitating proteids, forming coloured precipitates which are presumably salts of the dye base with the acidic proteid. If the base is a feeble one, then serum-albumin is often capable of decomposing the dye salt, combining with the acid and setting free the colour-base. The dye salt of a stronger base is also decomposed, but both the acid and the colour-base combine with the proteid. With salts of extremely strong basic dyes, no decomposition occurs, but the proteid combines directly with the salt; that is, the salts act as partially neutralised bases, and the coloured products formed are usually thrown out of solution. Nucleic acids readily combines with basic dyes.

J. J. S.

**Possible Combinations of Fat and Proteid.** By E. R. POSNER and WILLIAM J. GIES (*Amer. J. Physiol.*, 1902, 7, 331—339. Compare this vol., i, 331).—In connection with Nerking's work on fat-proteid compounds, it is concluded that many proteids (tendon-mucoid, osseo-mucoid, chondro-mucoid, collagen, gelatin, elastin, edestin, myosin, egg-albumin, Witte's peptone, somatose, chloralbacid) of the simple, compound, and albuminoid types, prepared by the best methods, are not

'fat proteid' compounds, nor do they bear any resemblance to lecith-albumins.  
W. D. H.

**Action of Alkali Hydroxides on Egg-Albumin.** By CARL PAAL (*Ber.*, 1902, 35, 2195—2206).—The action of alkali hydroxides on egg-albumin has been reinvestigated, and the acids which are precipitated on neutralising the alkaline solutions have been studied.

*Protalbic acid* is prepared by heating albumin at 100° with 3 per cent. aqueous sodium hydroxide for one hour; during this process, ammonia is evolved, and the solid nearly entirely dissolves; on acidifying with acetic acid, the acid is precipitated, and is freed from salts by dialysis. When freed from water by washing with alcohol, and subsequent drying, it forms a white powder, easily soluble in aqueous acetone or acetic acid, and both in alkalis and acids. A series of analyses of the acid and its salts gives C=53.5—54, H=7.3—7.5, N=14.3—14.6 per cent; a small quantity of sulphur is also present. The *sodium* salt, prepared by dissolving the acid in excess of sodium hydroxide, and removing the excess of alkali by dialysis, is a white, amorphous powder; the *potassium*, *calcium*, and *barium* salts are similar; the *zinc*, *ferric*, *mercuric*, and *silver* salts, prepared by precipitation, were all analysed.

*Lysalbic acid* is contained in the mother liquors, from which protalbic acid has separated, and is isolated by evaporating the solution to a small bulk, and then acidifying with sulphuric acid; it may be purified by pouring its concentrated aqueous solution into alcohol, and is a white powder forming an acid solution and giving the biuret reaction. Its composition is C=50.5—51.2, H=6.6—6.9, N=15.1—15.7 per cent.; a small quantity of sulphur was present; cryoscopic determinations of the mol. weight of the acid dried over sulphuric acid gave 818—838, and of the acid dried at 100°, 1171—1187. The *sodium* salt is an amorphous, soluble powder, the *ferric* salt a red powder, and the *silver* salt a yellow powder.  
K. J. P. O.

**Action of Dilute Nitric Acid on Casein and the Formation of Hydroxyglutaric Acid.** By JOSEF HABERMANN and R. EHRENFELD (*Zeit. physiol. Chem.*, 1902, 35, 231—245).—When the liquid obtained by heating casein with dilute nitric acid for several hours at 70° is extracted with ether and the solvent distilled off, there is left a crystalline residue, consisting chiefly of oxalic acid, but containing also hydroxyglutaric acid, which was purified by conversion into its zinc salt and recrystallisation of the latter, and a yellow, oily substance which accumulated in the mother liquors from the zinc hydroxyglutarate, and was eventually obtained in the form of reddish-yellow, crystalline nodules. This is volatile in steam, and is probably a nitro-derivative of a higher fatty acid. The ethereal residue referred to had a strong odour of leucic acid, but this, if present, could not be isolated. The original liquid, when distilled with steam, furnished a mixture of acetic and benzoic acids. No xanthoproteic acid was formed.  
T. A. H.

**Fibroin and Gelatin of Silk.** By EMIL FISCHER and ALADAR SKITA (*Zeit. physiol. Chem.*, 1902, 35, 221—226. Compare Wetzel, Abstr., 1899, i, 466; Fischer and Skita, Abstr., 1901, i, 783).—In addition to the monoamino-acids previously obtained by the hydrolysis of silk-fibroin with hydrochloric acid, the authors have now isolated by their usual method (Abstr., 1901, i, 192) serine 1·6 per cent., arginine 1 per cent., and probably histidine and lysine. When silk-gelatin is hydrolysed by boiling with dilute sulphuric acid, there are formed tyrosine, *i*-serine, arginine 4 per cent., lysine, glycine 0·1 per cent., *d*-alanine 5 per cent., and a seventh amino-acid, not yet identified, which differs from phenylalanine in being soluble in concentrated hydrochloric acid. The methods adopted for the separation of the acids were those of Fischer and of Kossel (Abstr., 1899, i, 833).

T. A. H.

**Antipeptone. II.** By MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1902, 35, 164—191. Compare Abstr., 1901, i, 57).—Antipeptone, although readily hydrolysed by alkalis, is relatively stable in the presence of trypsin.

The two acids previously described are most readily separated by the aid of their iron compounds. *β*-Antipeptone,  $C_{11}H_{19}O_5N_3$ , which is first precipitated as its iron compound, is a monobasic acid and has  $[\alpha]_D - 21·43^\circ$  at  $16^\circ$ . *α*-Antipeptone,  $C_{10}H_{17}O_5N_3$ , is also a monobasic acid; it yields an iron derivative which is more readily soluble than that of its isomeride, and has  $[\alpha]_D - 18·45$  or  $-19·69$ . Both compounds are snow-white powders only sparingly soluble in 96 per cent. alcohol, but readily so in phenol. The solutions have an acid reduction, whereas solutions of the sodium and barium salts give an alkaline reaction. They slowly decompose when heated at  $100^\circ$ . With Millon's reagent, Molisch's reagent, lead acetate, metaphosphoric acid, potassium ferrocyanide, or acetic acid, no characteristic reactions are given. They both give the biuret test and also yield precipitates with picric acid, mercuric chloride, or phosphotungstic acid. Decomposition of *α*-antipeptone with stannous chloride and hydrochloric acid gives rise to lysatinine, aminosuccinic acid, and lysine; the *β*-compound when treated similarly yields the same bases and glutamic acid. Peptone prepared from gelatin has a much higher molecular weight than the antipeptones and on decomposition with stannous sulphate and sulphuric acid yields arginine, lysine, glutamic acid, and glycine.

J. J. S.

**Hydrogenases of the Blood and the Catalytic Properties of Fibrin.** By M. EMM. POZZI-ESCOT (*Bull. Soc. Chim.*, 1902, [iii], 27, 459—460).—When the action of fibrin which has been digested in glycerol or alcohol for 48 hours is compared with that of fibrin obtained from blood and rapidly washed with water, with respect to its power of liberating oxygen from hydrogen peroxide, it is found that the fibrin which has been obtained in the former manner is less active than the latter, and that the liquid in which the fibrin was digested exhibits the properties of the hydrogenases. From this, the author



concludes that the above property of fibrin is due to its retention of hydrogenising diastases. A. F.

**Influence of Heat on Enzymes.** By S. P. BEEBE (*Amer. J. Physiol.*, 1902, 7, 295—300).—No evidence was obtained of marked changes in the physical character of enzyme solutions which had been subjected to a temperature of about 40°. W. D. H.

**The Inactivity of Lipase towards the Salts of Certain Acid Ethers considered in the Light of the Theory of Electrolytic Dissociation.** By J. H. KASTLE (*Amer. Chem. J.*, 1902, 27, 481—486).—Diethyl fumarate, diethyl oxalate, diethyl phthalate, ethyl oxamate, and ethyl *p*-sulphoaminobenzoate are easily hydrolysed by lipase, but no hydrolysis takes place with sodium ethyl fumarate, potassium ethyl oxalate, barium ethyl phthalate, diethyl *p*-nitrosulphobenzoate, barium or potassium *p*-sulphonitrobenzoate, ethyl *p*-sulphobenzoate, or barium or potassium ethyl sulphate.

From the results so far obtained on the hydrolysis by ferments, it appears that when the ester is electrolytically dissociated no hydrolysis takes place; this indicates that hydrolysis is preceded by combination of the hydrolyte with the enzyme and the combination cannot take place with ions, but only with undissociated molecules. J. McC.

**Chemical Nature of Pepsin and other Digestive Enzymes.** By HANS FRIEDENTHAL and S. MIYAMOTA (*Chem. Centr.*, 1902, i, 1117—1118, 1169; from *Centr. Physiol.*, 15, 785—786, 16, 1).—The nucleo-proteid material precipitable from dog's gastric juice can be broken up, and the products, which contain neither proteid nor nucleic acid, have peptic activity. The substance or substances which produce the effect are not dialysable, and are therefore of high molecular weight; they contain less ash than the original material. The zymophore group of the pepsin molecule is not proteid, which is against the view expressed by Pekelharing. W. D. H.

**Jacquemase, a New Reducing Diastase Extracted from the Japanese Koji, and Secreted by "Eurotium Oryzae."** By M. EMM. POZZI-ESCOT (*Bull. Soc. Chim.*, 1902, [iii], 27, 557—560).—The author shows that the taka diastase, extracted from koji, although possessing reducing properties, is not the same as philothion; in particular, it does not yield hydrogen sulphide with sulphur. For this new class of reducing diastases, the author proposes the name reductases. A. F.

**New Diastases in Urine.** By M. EMM. POZZI-ESCOT (*Ann. chim. anal.*, 1902, 7, 212—213).—The author has discovered a new class of diastases which he calls "reductases." Their presence in urine may be proved by first adding an antiseptic, sodium fluoride, and then hydrogen peroxide; if "reductases" are present, the latter will be decomposed.

For further particulars, the author refers to his other papers on the subject. L. DE K.

**Formation of Aromatic Mercury Compounds.** By OTTO DIMROTH (*Ber.*, 1902, 35, 2032—2045. Compare Dimroth, *Abstr.*, 1899, i, 154, 428; and Pesci, *Abstr.*, 1892, 1448; 1898, i, 648).—Aromatic compounds react with great ease with mercury acetate, thus, at 110—120°, benzene yields phenylmercury acetate. On boiling benzene, containing thiophen, with mercuric acetate, the latter forms a compound,  $\text{OAc}\cdot\text{Hg}\cdot\text{C}_6\text{H}_5\cdot\text{SH}_2\cdot\text{Hg}\cdot\text{OH}$ ; by this means, the whole of the thiophen can be removed from benzene, whilst at the same time but very little of the benzene forms a mercury derivative.

Naphthalene forms a mixture of mercury compounds, from which only  $\alpha$ -naphthylmercury acetate was isolated (Otto, *J. pr. Chem.*, 1870, [ii], 1, 185).

Nitrobenzene was heated with mercury acetate at 150°, and the resulting mixture treated with sodium chloride, when *o*-nitrophenylmercury chloride is obtained as yellowish leaflets melting at 181—182°, and with bromine in the presence of water, yielding *o*-bromonitrobenzene.

Aniline and an aqueous solution of mercuric acetate give mainly *p*-aminophenylmercury acetate (m. p. 166—167°), together with a small quantity of the isomeric ortho-compound,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{Hg}\cdot\text{OAc}$ , which crystallises in leaflets melting at 158—160°; its *acetyl* derivative, prepared by the use of acetic anhydride, crystallises in small leaflets melting at 156—158°, and is converted by bromine into *o*-bromoacetanilide. On adding sodium chloride to an acetic acid solution of *o*-aminophenylmercury acetate, *o*-aminophenylmercury chloride,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{HgCl}$ , is immediately formed, and crystallises in colourless leaflets; *p*-aminophenylmercury acetate, on the other hand, only yields the corresponding chloride in the absence of acetic acid; this chloride crystallises in leaflets melting and decomposing at 188°; in the presence of acetic acid, an insoluble, amorphous, polymeric chloride is obtained.

With sodium thiosulphate, *p*-aminophenylmercury acetate or chloride yields an unstable compound,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{Hg}\cdot\text{S}_2\text{O}_3\text{Na}$ , which crystallises in lustrous leaflets melting and decomposing at 95°, and decomposes very readily on warming with water into *p*-mercurianiline,  $(\text{NH}_2\cdot\text{C}_6\text{H}_4)_2\text{Hg}$ , and sodium mercury thiosulphate.

The compound obtained by the action of sodium hydroxide on *p*-aminophenylmercury acetate is regarded by the author as *p*-mercuriphenylimine,  $\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{Hg}$ ; on treatment with methyl iodide, it is converted into *iodomercuriphenyltrimethylammonium iodide*,  $\text{IHg}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{I}$ ; the latter crystallises in greenish-yellow prisms melting at 139—140° and readily decomposes into mercuric iodide and *p*-mercuriphenyltrimethylammonium iodide,  $\text{Hg}(\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{I})_2$ .

Dimethylaniline reacts with mercuric acetate, forming *p*-dimethylaminophenylmercury acetate.

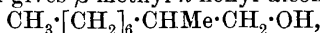
Attention is drawn to the fact that mercury derivatives of anilines, in which the mercury is attached to the nitrogen, for example,  $\text{Hg}(\text{NHPh})_2$ , are immediately decomposed by hydrogen sulphide, whereas *p*-aminophenylmercury acetate, &c., are unchanged by this agent.

K. J. P. O.

## Organic Chemistry.

**Synthesis of Ethyl Alcohol.** By P. FRITZSCHE (*J. pr. Chem.*, 1902, [ii], 65, 597—600. Compare Berthelot, *Abstr.*, 1899, i, 471).—A defence of Hennel. G. Y.

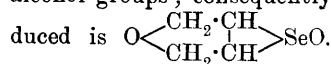
**Action of Alcohols on the Sodium Compounds of other Alcohols.** By MARCEL GUERBET (*Compt. rend.*, 1902, 135, 172—175).—By heating together in a sealed tube to 230° a mixture of heptyl alcohol, ethyl alcohol, and sodium, there is formed *n*-nonyl alcohol (b. p. 212—214°). In the same way, a mixture of heptyl alcohol and *n*-propyl alcohol gives  $\beta$ -methyl-*n*-nonyl alcohol,



as a colourless oil which boils at 221—223°, and has the sp. gr. 0·8457 at 0° and 0·8333 at 15°. Its acetate is a colourless oil, with an odour resembling that of lemon; it boils at 238—240° and has the sp. gr. 0·8812 at 0° and 0·8705 at 15°. When the alcohol is heated at 250° with fused potassium hydroxide, the corresponding acid,  $\text{C}_{10}\text{H}_{20}\text{O}_2$ , is formed as a colourless oil which boils at 261—265°, and has a sp. gr. 0·9127 at 0°; it gives an amide which melts at 76°. The constitution of the acid was found from the oxidation products—carbon dioxide, acetic, heptic, and octoic acids. From the constitution of the alcohol, it is evident that the condensation has taken place at the expense of the hydroxyl of the heptyl alcohol. J. McC.

**Action of Selenyl Chloride on Erythritol.** By CAMILLE CHABRIÉ and R. JACOB (*Compt. rend.*, 1902, 134, 1507—1509).—When erythritol is heated with selenyl chloride, hydrogen chloride is given off at 68°. When the mixture is heated for an hour at 100°, a yellowish oil is obtained which does not solidify at -15° and is easily soluble in water or alcohol. When the mixture is heated at 178°, then allowed to cool, and filtered, colourless, needle-shaped crystals separate which melt at 155°. The composition of these is represented by the formula  $\text{C}_4\text{H}_6\text{O}_4\text{Se}$ , from which it is evident that the erythritol has lost one mol. of water in the reaction, and two atoms of hydrogen have been replaced by the selenyl group with simultaneous production of two mols. of hydrogen chloride.

Glycol, when heated with selenyl chloride, gives off water, but inositol does not, and since the former contains only primary alcohol groups and the latter only secondary alcohol groups, it is concluded that the mol. of water is eliminated from the primary alcohol groups, and the hydrogen of the evolved hydrogen chloride from the secondary alcohol groups; consequently, the constitution of the compound produced is



J. McC.

**Ethyl Acetoacetate and its Derivatives.** By ERNST VON MEYER [and, in part, by ALFR. FRIESSNER and TH. VON FINDEISEN] (*J. pr. Chem.*, 1902, [ii], 65, 528—533).—In the preparation of ethyl

acetoacetate by the action of sodium on ethyl acetate, the amount of hydrogen evolved is almost proportional to the yield of ester. It is found impossible to increase the yield beyond 40 per cent. of the theoretical.

The action of *p*-toluenesulphonic chloride on ethyl sodioacetoacetate leads to the formation of sodium *p*-toluenesulphinate and ethyl  $\alpha$ -chloroacetoacetate, and also to ethyl *p*-toluenesulphoacetoacetate, probably  $C_7H_7 \cdot SO_2 \cdot O \cdot CMe \cdot CH \cdot CO_2Et$ , which reacts with unchanged ethylsodioacetoacetate to form ethyl sodio-*p*-toluenesulphoacetoacetate, and on addition of water is decomposed into sodium *p*-toluenesulphonate and ethyl acetoacetate. Acetylation of ethyl acetylsuccinate by sodium and acetyl chloride results in the formation of ethyl *as*-diacetylsuccinate, which boils at 275° and with phenylhydrazine yields a *pyrazolone* derivative,  $\begin{matrix} NPh-CO \\ | \\ N=CMe \end{matrix} > CAc \cdot CH_2 \cdot CO_2Et$ , which forms white crystals and melts at 79°.

G. Y.

**Crystallography of Methyl Methylcamphocarboxylate, Ethyl Methylcamphocarboxylate, Methylcamphoronitrile, and Methylcamphorimide.** By JULES MINGUIN (*Bull. Soc. Chim.*, 1902, [iii], 27, 681—683).—Methyl methylcamphocarboxylate forms monoclinic prisms [ $a : b : c = 0.70686 : 1 : 0.6142$ ;  $\beta = 115^\circ$ ]. Ethyl methylcamphocarboxylate crystallises in rhombic prisms [ $a : b : c = 0.88213 : 1 : 0.60063$ ]. Methylcamphoronitrile crystallises in rhombic prisms [ $a : b : c = 0.63707 : 1 : 0.33636$ ]. Methylcamphorimide forms small crystals apparently belonging to the anorthic system. A. F.

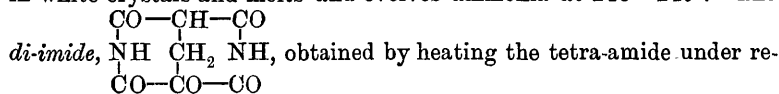
**Action of Ammonia on Halogen-substituted Malonic Acids.** By O. LUTZ (*Ber.*, 1902, 35, 2549—2554. Compare this vol., i, 596).—Bromomalonic acid can be prepared advantageously by direct bromination in acetic acid solution; the product is evaporated over sodium hydroxide in a vacuum desiccator and recrystallised from a little acetone (over sodium hydroxide) or much benzene (over paraffin) in a vacuum desiccator. Unlike the monohalogen-substituted succinic acids, chloro- and bromo-malonic acids yield aminomalonic acid, and not tartronaminic acid, when treated with ammonia. T. M. L.

**$\alpha$ -Hydroxyglutaric Acid and the Action of Bromine on Glutaric Acid.** By V. PAOLINI (*Gazzetta*, 1902, 32, i, 402—409).—When glutaric acid is heated in a sealed tube with bromine, it yields  $\alpha$ -bromoglutaric acid, which then splits up in two distinct ways: (1) Hydrogen bromide is given off with the formation of pentane-2 : 5-olidoic acid, and the latter becomes hydrolysed to  $\alpha$ -hydroxyglutaric acid. (2) Part of the  $\alpha$ -bromoglutaric acid loses carbon dioxide, giving  $\gamma$ -bromobutyric acid, which gives up hydrogen bromide yielding  $\gamma$ -butyrolactone, and this, on hydrolysis, forms succinic acid.

The dehydration of  $\alpha$ -hydroxyglutaric acid yields pentane-2 : 5-olidoic acid and also glutaconic acid. T. H. P.

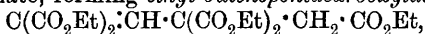
**Action of Amino-bases on Ethyl Dicarboxyglutarate and or Ethyl Chloroacetate on Ethyl Dicarboxyglutaconate.** By MAX GUTHZEIT and CARL JAHN (*J. pr. Chem.*, 1902, [ii], 66, 1—15).—Ethyl di-

carboxyglutarate, when treated with ammonia or aniline, yields the corresponding tetra-amide or tetra-anilide. The *tetra-amide* separates from water in white crystals and melts and evolves ammonia at 248—249°. The



duced pressure at 250°, crystallises from alcohol, decomposes at about 200°, and forms a crystalline *silver* salt. The *tetra-anilide* separates from alcohol as a white, crystalline powder and melts at 255—256°.

Ethyl chloroacetate reacts with the disodium derivative of ethyl dicarboxyglutaconate, forming *ethyl butenepentacarboxylate*,



which is a yellow, viscous oil boiling at 222—225° under 16 mm. pressure, and is split up by ammonia, yielding ethyl aminoethylenedicarboxylate and the triamide of ethanetricarboxylic acid. The ethyl aminoethylenedicarboxylate obtained by the authors melts at 56—57°, and is probably an isomeride of that obtained by Ruhemann and Morrell (Trans., 1891, 59, 747).

*Ethanetricarboxyltriamide* separates from alcohol as a white, microcrystalline powder and melts and decomposes at 225°.

*Ethyl butanepentacarboxylate*, obtained by reducing the corresponding butene compound with zinc dust and acetic acid, is a colourless, thick oil which boils at 220—240° under 12 mm. pressure and is not split up by aqueous ammonia.

R. H. P.

**Reaction between Chloral Hydrate and Alkali.** By WILHELM BÖTTGER and ARTHUR KÖTZ (*J. pr. Chem.*, 1902, [ii], 65, 481—499. Compare Reicher, *Rec. trav. Chim.*, 1885, 4, 347).—With a slight excess of alkali present at the commencement, the reaction between chloral hydrate and alkali is apparently bimolecular; the presence of slight excess of chloral hydrate diminishes the rate of reaction, which becomes unimolecular. The end of the reaction is complicated by the presence of chlorine ions. The production of hydrogen and chlorine ions in a neutral solution of chloral hydrate is caused by contact with platinised platinum foil; non-platinised platinum has little or no effect. Addition of hydrochloric acid to the solution tends to diminish the rate of the reaction. This reaction takes place also with the sodium salts of trichloroacetic, nitro-, *m*-cyano-, *m*-chloro-, *o*-chloro-, and bromo-benzoic acids and of dibromosuccinic acid, the aqueous solution becoming acid and giving the reactions of the ions,  $\text{NO}_2'$ ,  $\text{CN}'$ ,  $\text{Cl}'$ ,  $\text{Br}'$ .

The hydrolysis of chloroform in aqueous solution and of ethyl acetate in alkaline solution is accelerated by the presence of platinised platinum (compare Kohlrausch, Abstr., 1900, ii, 408).

G. Y.

**Transformation of Ketones into  $\alpha$ -Diketones. VI.** By GIACOMO PONZIO and V. BORELLI (*Gazzetta*, 1902, 32, i, 419—424).—By the action of hydroxylamine on a dichloroketone prepared from dipropyl ketone by the successive action of phosphorus pentachloride, sodium hydroxide, and hypochlorous acid, Faworski and Desbout (Abstr., 1895, i, 496) obtained a substance melting at 129° which they regarded as propionylbutyryldioxime. This compound, however, prepared by Fileti

and Ponzio (Abstr., 1897, i, 317) by the action of hydroxylamine hydrochloride on the product obtained by oxidising dipropyl ketone with nitric acid, was found to melt at 167—168°. The authors have now prepared this substance from propionylbutyryl and find that it melts at 167.5°.

*Propionylbutyryl*,  $\text{CH}_2\text{Me}\cdot\text{CO}\cdot\text{COPr}^a$ , obtained by oxidising dipropyl ketone by means of nitric acid, is a yellow liquid which boils at 147° under 732 mm. pressure and is readily volatile in steam. Its *phenylhydrazone*,  $\text{CH}_2\text{Me}\cdot\text{C}(\text{N}_2\text{HPh})\cdot\text{COPr}^a$ , crystallises from dilute alcohol in straw-yellow prisms melting at 91.5°.

*isoNitrosodipropyl ketone*,  $\text{NOH}\cdot\text{CEt}\cdot\text{COPr}^a$ , obtained by the action of nitrous acid on dipropyl ketone, is a dense, colourless liquid boiling at 145° under a pressure of 60 mm.

*Propionylbutyryl- $\alpha$ -hydrazone- $\beta$ -oxime* crystallises from dilute alcohol in almost white prisms which melt at 135° and are soluble in ether.

T. H. P.

**Formation of Ketoximes.** By LUIGI FRANCESCONI and A. MILESI (*Gazzetta*, 1902, 32, i, 425—436).—The authors have studied the reaction between acetoxime and an acid, which they find to be very rapid. In about an hour, a condition of equilibrium is reached which is independent of the nature of the acid, and is represented approximately by the equation: Acetoxime (2/3) + acid (2/3) + water = acetone (1/3) + hydroxylamine salt (1/3). These results not being in agreement with Prati's experiments (Abstr., 1895, ii, 259) on the inverse reaction to the above, the latter were repeated, the results obtained being in complete accord with those of the authors.

Experiments made with the help of methyl acetate to determine the extent to which salts of hydroxylamine undergo hydrolysis in dilute solution show that the proportion of acid set free in this manner is very slight. Conductivity measurements confirm this result.

T. H. P.

**Isolation of Ketoses. II.** By CARL NEUBERG (*Ber.*, 1902, 35, 2626—2633. Compare this vol., i, 264).—In phenylmethylhydrazine, the author has found a reagent which forms osazones only with the ketoses of the *i*-erythritol, adonitol, xylitol, and dulcitol series, and not with the aldoses (compare *loc. cit.*).

The solutions containing ketoses were obtained by oxidising the polyhydric alcohols either with nitric acid, sodium hypobromite, hydrogen peroxide and ferrous sulphate, or lead dioxide and hydrochloric acid.

*i*-Erythrosephenylmethylosazone,  $\text{C}_{18}\text{H}_{22}\text{O}_2\text{N}_4$ , was prepared by oxidising erythritol with hydrogen peroxide and ferrous sulphate, and after neutralising and evaporating to dryness taking up the residue with alcohol and adding the hydrazine and acetic acid; the osazone forms yellowish crystals melting at 158—159°; at most, 3 grams of osazone were obtained from 12 grams of erythritol.

*i*-Xyloketosephenylmethylosazone,  $\text{C}_{10}\text{H}_{24}\text{O}_3\text{N}_4$ , was prepared from the product of oxidation of xylitol with lead dioxide and hydrochloric acid; it was formed in very small quantity and crystallised in yellow needles melting at 173°.

i-*Riboketosephenylmethylosazone*,  $C_{19}H_{24}O_3N_4$ , crystallises in slender needles, softening at  $171^\circ$  and melting at  $175^\circ$ .

i-*Tagatosephenylmethylosazone*,  $C_{20}H_{26}O_4N_4$ , prepared from dulcitol, melts at  $148-150^\circ$  and is optically inactive, as are all the osazones just described.

This method has also been used, in order to determine whether ketoses or aldoses are formed, when glycolaldehyde or "glycerose" is caused to condense to higher sugars by the action of alkalis. The sugar obtained from glycolaldehyde did not yield an osazone with phenylmethylhydrazine, but only with phenylhydrazine; thus an aldo- and not a keto-tetrose was present. The hexose obtained from "glycerose," gave a phenylmethylosazone,  $C_{20}H_{26}O_4N_4$ , crystallising in reddish-yellow needles melting at  $158^\circ$  and identical with the osazone obtained from *r*-fructose; "acrose" is then *r*-fructose.

On treating "formose," obtained from formaldehyde, in a similar manner, no hexo-osazone was produced, but a phenylmethylpentosazone,  $C_{19}H_{22}O_3N_4$ , which crystallised in yellow needles melting at  $137^\circ$  and not identical with any known pentosazone.

K. J. P. O.

Two new Sugars contained in Manna, Manneotetrose, and Manninotriose. By CHARLES TANRET (*Compt. rend.*, 1902, 134, 1586-1589).—Manna (the exudation of *Fraxinus ornus*) contains, besides mannitol, two sugars, manneotetrose and manninotriose, forming together about a sixth of the manna. To isolate these sugars, the manna is extracted with water and the mannitol precipitated with alcohol; from the mother liquors the sugars are obtained as barium compounds, which are fractionally decomposed by carbon dioxide and then fractionally crystallised from alcohol.

*Manneotetrose*,  $C_{24}H_{42}O_{21}$ , forms small, monoclinic crystals, with  $4.5H_2O$ , which change at  $150^\circ$  and melt at  $167^\circ$ ; the hydrated sugar has  $[\alpha]_D +133.85^\circ$ , and the anhydrous  $[\alpha]_D +150^\circ$ ; it does not reduce Fehling's solution. By acetic acid, it is converted into the manninotriose, above mentioned, and lævulose; the enzymes, emulsin, diastase, and invertase have a similar action. With lead acetate in the presence of ammonia, the compound  $C_{24}H_{34}O_{22}Pb_4$  is formed as a precipitate; the barium derivative,  $(C_{24}H_{42}O_{21})_2(BaO)_3$ , is prepared by addition of baryta in the presence of alcohol to an aqueous solution. Manneotetrose is partially fermented by yeast.

*Manninotriose*,  $C_{18}H_{32}O_{16}$ , is best obtained pure by treating the mixture of manneotetrose and manninotriose, obtained from manna, with 20 per cent. acetic acid which converts the tetrose into the triose; after extracting the acid with ether, the sugar is obtained by evaporating and precipitating with alcohol; it has  $[\alpha]_D +167^\circ$ , reduces Fehling's solution, and decomposes at  $150^\circ$ ; by mineral acids, it is converted into galactose (2 mols.) and dextrose (1 mol.). When oxidised with bromine water, it yields manninitronic acid,  $C_{18}H_{32}O_{17}$ , which is hydrolysed by acids to galactose and gluconic acid.

K. J. P. O.

Betaine Aurichloride. By RICHARD WILLSTÄTTER (*Ber.*, 1902, 35, 2700-2703).—In reply to E. Fischer (this vol., i, 428), it is shown

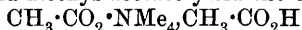
that betaine aurichloride occurs in two modifications. When crystallised from very dilute hydrochloric acid, it is obtained in octahedra which melt and decompose at 200—209°, and when recrystallised from hydrochloric acid are converted into the rhombic modification melting at 248—250° described by Fischer (*loc. cit.*).

A third modification containing water of crystallisation is apparently obtained when the aurichloride is crystallised from water.

R. H. P.

**The Action of Esters of Organic Acids on Tertiary Bases.** By RICHARD WILLSTÄTTER and WALTER KAHN (*Ber.*, 1902, 35, 2757—2761).—Tetramethylammonium benzoate (Lawson and Collie, *Trans.*, 1888, 53, 631) is obtained when methyl benzoate is warmed with anhydrous trimethylamine in sealed tubes for 7 hours at 160°; it melts at about 192°.

Trimethylamine and methyl acetate yield the compound



in the form of hygroscopic crystals melting at 90° and decomposing at 195°. Methyl oxalate combines with one mol. of trimethylamine only, yielding the compound  $\text{CO}_2\text{Me} \cdot \text{CO}_2 \cdot \text{NMe}_4$ , which softens at 100°, melts at 125°, and begins to decompose at 140°.

Methyl phthalate and trimethylamine yield *methyl tetramethylammonium phthalate*,  $\text{CO}_2\text{Me} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{NMe}_4$ , in the form of colourless plates softening at 132°, and completely melting at 150°. J. J. S.

**Mechanism of the Synthesis of Leucine.** By A. VILA and E. VALLÉE (*Compt. rend.*, 1902, 134, 1594—1597. Compare this vol., i, 207).—This paper is a more detailed account of the preparation and properties of the substances obtained by Étard and Vila (*loc. cit.*) in the synthesis of leucine from active valeraldehyde,  $\text{CH}_2\text{Me} \cdot \text{CHMe} \cdot \text{CHO}$ . Valeraldehyde-ammonia,  $\text{C}_5\text{H}_{10}\text{O} \cdot \text{NH}_3$ , is obtained as an oil by exposing the hydrate over baryta; it absorbs water from the air, re-forming crystals of the hydrate. The nitrile, prepared from the ammonia derivative, crystallises in long needles melting at 58°; its mol. weight (in benzene) corresponds with that required for the formula  $\text{C}_{15}\text{H}_{21}\text{N}_3$  (compare *loc. cit.*); on passing hydrogen chloride into its ethereal solution, a crystalline *hydrochloride* is formed melting at 86°. K. J. P. O.

**Structurally Isomeric Mercury Cyanurates.** By ARTHUR HANTZSCH (*Ber.*, 1902, 35, 2717—2723).—*Mercuric cyanurate*,  $(\text{C}_3\text{N}_3)_3(\text{Ohg})_3 \cdot 2\text{H}_2\text{O}$ , obtained when a solution of trisodium cyanurate or a solution of cyanuric acid with three mols. of sodium hydroxide is precipitated at 0° with a solution of mercuric acetate or chloride, is decomposed by alkalis with the separation of mercuric oxide.

*Mercuric isocyanurate*,  $(\text{CO})_3(\text{Nhg})_3 \cdot 2\text{H}_2\text{O}$ , obtained in a similar manner at 100°, is indifferent to alkalis and can be boiled with sodium hydroxide without losing its white colour. R. H. P.

**Thiocyano-compounds of Cadmium.** By HERMANN GROSSMANN (*Ber.*, 1902, 35, 2665—2669).—Cadmium thiocyanate,  $\text{Cd}(\text{SCN})_2$ , can be prepared from barium thiocyanate and cadmium sulphate, and



forms crystalline crusts. A *compound*,  $\text{Cd}(\text{SCN})_2 \cdot \text{NH}_3$ , is formed when cadmium hydroxide is boiled with ammonium thiocyanate; it forms large, monoclinic crystals, and is decomposed by water; addition of ammonia to its aqueous solution converts it into the *compound*  $\text{Cd}(\text{SCN})_2 \cdot 2\text{NH}_3$ . In the mother liquor from the latter, an *ammonium cadmiothiocyanate*,  $(\text{NH}_4)_2\text{Cd}(\text{SCN})_4 \cdot 2\text{H}_2\text{O}$ , is contained; it crystallises in monoclinic plates which melt in their water of crystallisation at  $25^\circ$ . The *potassium* salt, prepared from the ammonium salt, crystallises in octahedra, the *rubidium* salt in six-sided leaflets. *Rubidium thiocyanate*,  $\text{RbSCN}$ , crystallises in long, prismatic needles. The *sodium* salt,  $\text{NaCd}(\text{SCN})_3 \cdot 3\text{H}_2\text{O}$ , prepared from a solution of cadmium thiocyanate and sodium thiocyanate, forms hexagonal plates. The *barium cadmium* double salt,  $4\text{Ba}(\text{SCN})_2 \cdot \text{Cd}(\text{SCN})_2 \cdot 10\text{H}_2\text{O}$ , crystallises in large, four-sided plates.

K. J. P. O.

### Hofmann's Reaction. Conversion of Amides into Amines.

By CARL GRAEBE and SERGE ROSTOVZEFF (*Ber.*, 1902, 35, 2747—2752).—Comparative experiments have proved that sodium hypochlorite is a more valuable reagent than the hypobromite in Hofmann's reaction, mainly on account of the fact that it is more stable. The experiments were carried out with phthalimide and its chloro-derivatives and also with *o*-benzylbenzamide. The Hofmann reaction is probably to be represented as taking place in the following stages: 1,  $\text{X} \cdot \text{CO} \cdot \text{NH}_2 + \text{NaClO} = \text{X} \cdot \text{CO} \cdot \text{NNaCl} + \text{H}_2\text{O}$ ; 2,  $\text{X} \cdot \text{CO} \cdot \text{NNaCl} \rightarrow \text{X} \cdot \text{NNa} \cdot \text{COCl}$ ; 3a, when excess of alkali is present,  $\text{X} \cdot \text{NNa} \cdot \text{COCl} + 2\text{NaOH} = \text{X} \cdot \text{NH}_2 + \text{NaCl} + \text{Na}_2\text{CO}_3$  or 3b, when excess of alkali is not present,  $2\text{X} \cdot \text{NNa} \cdot \text{COCl} + \text{H}_2\text{O} = (\text{X} \cdot \text{NH})_2\text{CO} + 2\text{NaCl} + \text{CO}_2$ . As proof of this, the authors find that a theoretical yield of diphenylcarbamide is obtained when benzoylchloroamide (1 mol.) is left in contact with sodium hydroxide (1 mol.).

The third stage of the reaction can proceed in a different manner when the formation of a stable ring is possible, 3c,  $\text{ONa} \cdot \text{C}_6\text{H}_4 \cdot \text{NNa} \cdot \text{COCl} = \text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{NNa} \\ \text{O} \end{smallmatrix} \right\rangle \text{CO} + \text{NaCl}$ . This reaction is typified in the case of salicylamide, which, when treated with sodium hypochlorite in the presence of excess of alkali, yields oxycarbanil. The amide of methylsalicylic acid under similar conditions yields anisidine.

J. J. S.

**Attempts to prepare Thionic and Dithionic Acids in the Fatty Series.** By C. V. JØRGENSEN (*J. pr. Chem.*, 1902, [ii], 66, 28—46).—The nitriles, when treated with sodium hydrogen sulphide in aqueous or dilute alcoholic solution, yield only the sodium salts of the corresponding fatty acids, and when treated with an alcoholic solution of sodium hydrogen sulphide, yield thioamides. The salt obtained by Dupré (*Abstr.*, 1878, 568) in an analogous manner in the presence of an excess of hydrogen sulphide is sodium thiosulphate.

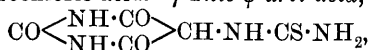
Thioacetamide, when treated with sodium ethoxide, yields sodium sulphide, alcohol, acetonitrile, mercaptan, sodium thiosulphate and acetate, and ammonia. Methylthioacetanilide is hydrolysed by dilute alcoholic sodium hydroxide, yielding methylaniline and sodium thio-

sulphate and sulphide, but is not affected by an alcoholic solution of sodium hydrogen sulphide. Ethylisothioacetanilide reacts with carbon disulphide at 180—200°, yielding ethyl mercaptan, aniline, and an undetermined compound, which crystallises from alcohol and melts at 148°.

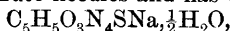
Carbon disulphide reacts with sodium zinc methyl at 110°, forming isopropyl mercaptan and several inorganic salts. Attempts to prepare thioacetyl chloride (i) by action of phosphorus pentasulphide on acetyl chloride, and (ii) by heating the salt,  $\text{CSMe}\cdot\text{NH}_2\cdot\text{HCl}$ , were failures. The action of acetyl chloride on thioacetamide yielded a yellow, crystalline mass, which is probably an additive compound of both reagents.

R. H. P.

**Conversion of *iso*Uric Acid into Uric Acid and Thioxanthine.** By EMIL FISCHER and HERMANN TÜLLNER (*Ber.*, 1902, 35, 2563—2571).—*iso*Uric acid is converted completely into uric acid by heating with 20 per cent. hydrochloric acid. *γ*-Thio *ψ*-uric acid,

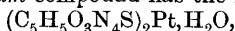


or  $\text{CO} \begin{array}{c} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{array} \text{CH}\cdot\text{NH}\cdot\text{C}(\text{SH})\cdot\text{NH}$ , is readily prepared by the action of ammonium sulphide on *isouric* acid and can be isolated by precipitating the barium salt with sulphuric acid and evaporating the filtrate under 20 mm. pressure; it forms minute, colourless needles, is exceedingly soluble in water, gradually decomposes in aqueous solution with formation of thioxanthine and sulphur, and decomposes when heated with liberation of gas. The *ammonium* salt crystallises in colourless, glistening needles or thin prisms, becomes dark and decomposes with liberation of gas at about 255°, and, unlike the *isourate*, does not become red when the aqueous solution is exposed to air. The *sodium* salt forms a paste of minute needles and has the composition



although the water of crystallisation could not be directly determined.

The *potassium* salt also forms very minute needles. The *barium* salt,  $(\text{C}_5\text{H}_5\text{O}_3\text{N}_4\text{S})_2\text{Ba}\cdot 3\text{H}_2\text{O}$ , crystallises from hot water in colourless prisms and begins to decompose at 109° before the water of crystallisation is lost. The *platinum* compound has the formula,



or perhaps  $(\text{C}_5\text{H}_4\text{O}_3\text{N}_4\text{S})_2\text{Pt}$ , and forms yellow, glistening crystals.

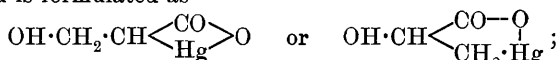
The conversion of *γ*-thio-*ψ*-uric acid into thioxanthine is readily brought about by heating the ammonium salt with 20 per cent. hydrochloric acid on a water-bath for half-an-hour.

T. M. L.

**Solubility of Prussian Blue under certain Conditions.** By CH. COFFIGNIER (*Bull. Soc. Chim.*, 1902, [iii], 27, 696—699).—When treated in the cold with hydrochloric acid, Prussian blue dissolves to a certain extent, furnishing a green solution; on heating, more of the blue passes into solution. If the solution contains more than 2 grams of Prussian blue per litre, a deposit of hydroferrocyanic acid separates on standing. On employing mixtures of equal volumes of hydrochloric acid and alcohols of the fatty series, a much larger quantity of

Prussian blue dissolves, the solutions being of a faint yellow to dark brown or reddish colour. In the case of hydrochloric acid and ethyl alcohol, the solutions containing 10 grams or more of Prussian blue per litre yield a deposit when kept, but with mixtures of hydrochloric acid and propyl or isobutyl alcohol, stable solutions can be obtained containing as much as 20 grams per litre. In the case of hydrochloric acid and amyl alcohol, as much as 40 grams per litre can be dissolved, but when the quantity exceeds 20 grams per litre, two liquid layers are produced. In all cases, the addition of a small quantity of water suffices to produce a blue precipitate. A. F.

**Organic Mercury Compounds.** By EINAR BIILMANN (*Ber.*, 1902, 35, 2571—2588).—Mercury acrylate is soluble both in acids and alkalis and is formulated as



it is also soluble in sodium chloride, perhaps with formation of  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{HgCl})\cdot\text{CO}_2\text{Na}$ , whilst potassium iodide gives mercuric iodide and potassium acrylate. Compounds of similar type are formed from crotonic acid, maleic acid, itaconic acid, and citraconic acid, whilst fumaric acid and mesaconic acid yield only normal mercury salts. Malonic acid and ethyl malonate yield compounds in which the hydrogen of the methylene group is replaced by mercury. Experiments with acetone, ethyl acetoacetate, and acetylacetone are also described. T. M. L.

**Optically Active Saturated Cyclic Hydrocarbons (Active Naphthenes).** By NICOLAI ZELINSKY (*Ber.*, 1902, 35, 2677—2682).—*d*-1:3-Dimethyl-3-cyclopentanol readily yields the corresponding *iodide*, which is laevorotatory and has  $\alpha_D - 2^\circ 39'$  ( $l = 0.25$  dm.). This substance is converted by reduction with zinc dust and acetic acid into active 1:3-dimethylcyclopentane,  $\text{CH}_2\left\langle\begin{array}{c}\text{CHMe}\cdot\text{CH}_2 \\ \text{CHMe}\cdot\text{CH}_2\end{array}\right\rangle$ , which boils at  $90.5-91^\circ$ , has a sp. gr.  $0.7497$  at  $16^\circ/4^\circ$ ,  $n$   $1.4110$  at  $18^\circ$ , and  $[\alpha]_D + 1.78^\circ$ . The stereoisomerism is due to the *cis-trans*-position of the methyl group. Apart from optical activity, this compound agrees in physical properties with the inactive hydrocarbon prepared from dimethyladipic acid.

Active 1-methyl-3-ethylcyclopentane,  $\text{C}_8\text{H}_{16}$ , is prepared from methyl-ethyl-3-cyclopentanol, and boils at  $120.5-121^\circ$ ; it has a sp. gr.  $0.7669$  at  $16^\circ/4^\circ$ ,  $n$   $1.4214$  at  $16^\circ$ , and  $[\alpha]_D + 4.34^\circ$ . In this case, two pairs of stereoisomerides are possible, the *cis-cis*- and the *cis-trans*-forms.

Active 1:3-dimethylcyclohexane,  $\text{C}_8\text{H}_{16}$ , boils at  $119.5-120^\circ$ , has a sp. gr.  $0.7661$  at  $26^\circ/4^\circ$ ,  $n$   $1.4218$  at  $26^\circ$ , and  $[\alpha]_D$  about  $+0.65^\circ$ . This hydrocarbon is derived from a crystalline 1:3-dimethylcyclohexanol, obtained by the fractionation of the liquid compound previously described (*Abstr.*, 1901, i, 660), which crystallises from light petroleum in very soft, fascicular aggregates of needles melting at  $71-72^\circ$ . It has  $[\alpha]_D + 7^\circ 15'$  and is stereoisomeric with the liquid alcohol previously obtained. The corresponding *iodide* boils at  $83.5-84.5^\circ$  under 16 mm. pressure.

3-Bromo-1-methyl-3-ethylcyclohexane, prepared from the corresponding optically active alcohol, boils at  $90-92^\circ$  under 20 mm. pressure, has a sp. gr. 1.1828 at  $16^\circ/4^\circ$ , and  $n_D + 1.02'$  ( $l = 0.25$  cm.).

Active 1-methyl-3-ethylcyclohexane boils at  $148-149^\circ$  (corr.), has a sp. gr. 0.7896 at  $17^\circ/4^\circ$ ,  $n_D 1.4353$  at  $17^\circ$ , and  $[\alpha]_D - 2.9^\circ$ .

It is noteworthy that the saturated cyclic hydrocarbons are much less optically active than the unsaturated hydrocarbons of the same class.

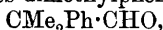
A. H.

**Migration of the Phenyl Group in Styrene and its Derivatives.** By MARC TIFFENEAU (*Compt. rend.*, 1902, 134, 1505-1507).—When subjected to the action of silver nitrate, the iodohydrin of diphenylethylene,  $\text{Ph}_2\text{C}:\text{CH}_2$ , gives deoxybenzoin,  $\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$ , the formation of which can only be explained by a migration of one of the phenyl groups.

Styrene iodohydrin, when treated with sulphuric acid, gives phenyl-acetaldehyde,  $\text{CPh}:\text{CH} \rightarrow \text{CH}_2\text{Ph}\cdot\text{CHO}$ , and since under the same conditions phenylmethyl glycol,  $\text{OH}\cdot\text{CPhMe}\cdot\text{CH}_2\cdot\text{OH}$ , gives hydratropic aldehyde,  $\text{CHMePh}\cdot\text{CHO}$ , it is concluded that in the action with sulphuric acid it is a hydrogen atom and not the phenyl group which migrates.

With silver nitrate, phenylpropylene iodohydrin gives phenyl-acetone, proving that the phenyl group migrates.

When treated with silver nitrate, the iodohydrin of phenylisobutylene,  $\text{Me}_2\text{C}:\text{CHPh}$ , gives dimethylphenylacetaldehyde,



and in this case it is quite certain that it is the phenyl group which changes its place.

The migration of the phenyl group gives an explanation of the different behaviour of these ethylene derivatives towards mercuric oxide and silver nitrate. In all cases, reaction takes place with the latter, but only when the phenyl group is substituted (by one or more methoxy-groups in *isosafrole*, *anethole*, and  *$\psi$ -anethole*) does reaction take place with mercuric oxide.

Finally, it has been proved that the tolyl group migrates more readily than does the phenyl radicle. Thus, the iodohydrin of *as*-phenyltolylethylene,  $\text{PhCH}_2\cdot\text{CPh}:\text{CH}_2$ , gives phenyl *p*-xylyl ketone,  $\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Me}$ .

J. McC.

**Styrenes. II.** By AUGUST KLAGES (*Ber.*, 1902, 35, 2633-2646. Compare this vol., i, 611).—Grignard (*Abstr.*, 1900, i, 382) has shown that a ketone (1 mol.) such as acetophenone reacts with methyl iodide (1 mol.) and magnesium (1 atom) forming the tertiary alcohol, phenyldimethylcarbinol. If, however, 2 mols. of the alkyl iodide and 2 atoms of magnesium are used and the mixture heated for several hours, an ethylene derivative is alone obtained, in this case,  $\beta$ -allylbenzene. This reaction appears to be perfectly general, except when two ortho-substituents are present, as in acetylmesitylene. By means of sodium and alcohol, the ethylene derivatives can be easily reduced to the corresponding saturated hydrocarbons.

Magnesium ethiodide and acetylmesitylene yield an *additive* pro-

duct,  $C_6H_2Me_3 \cdot CMeI \cdot O \cdot MgEt, OEt_2$ , which forms a crystalline powder and reacts violently with water, re-forming acetylmesitylene.

$\beta$ -Allylbenzene,  $CH_2 \cdot CPhMe$  (Tiffeneau, this vol., i, 433), is obtained when the additive compound prepared from magnesium methyl iodide and acetophenone is decomposed by water at a high temperature; unchanged acetophenone is always mixed with the hydrocarbon. It is also formed when phenyldimethylcarbinol is heated with magnesium methyl iodide (compare Tiffeneau, *loc. cit.*). The additive compound just mentioned is a lustrous, crystalline powder; when decomposed with dilute acid or ice-cold water, phenyldimethylcarbinol is alone formed; if the compound contains unchanged acetophenone, a mixture is produced which cannot be separated by distillation; the pure carbinol boils at  $93-94^\circ$  under 13 mm., and at  $202^\circ$  under the ordinary pressure, and has a sp. gr.  $0.9724$  at  $18.5^\circ/4^\circ$ .

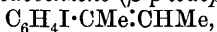
$\beta$ -Chloroisopropylbenzene,  $C_6H_5 \cdot CMe_2Cl$ , is prepared when hydrogen chloride is led into the carbinol cooled to  $0^\circ$ ; it is a colourless oil which evolves hydrogen chloride when heated and is converted into methylvinylbenzene on boiling with pyridine. The corresponding iodine derivative is an unstable, heavy oil; if its solution in acetic acid, or a solution of the carbinol in acetic acid containing hydriodic acid, is treated with zinc dust and the product neutralised and then distilled in steam, an oil, probably isopropylbenzene, distils, and a substance,  $C_{18}H_{22}$ , remains, which crystallises in needles melting at  $119-120^\circ$ , is stable towards permanganate and does not decolorise bromine; this substance is not identical with tetramethyldiphenylethane (Wallach, Abstr., 1900, i, 229), which melts at  $55-56^\circ$ ; it is possibly a cyclobutane derivative.

$\alpha$ -Iodoethylbenzene,  $C_6H_5 \cdot CHMeI$ , is prepared in a similar manner from phenylmethylcarbinol, and is a heavy, unstable oil; with zinc dust, it yields dimethyldibenzyl (m. p.  $126^\circ$ ).

On warming phenyldimethylcarbinol with syrupy phosphoric acid, it is converted into  $\beta$ -allylbenzene (b. p.  $165-168^\circ$ ), and a bimolecular  $\beta$ -allylbenzene,  $CPhMe \cdot CH \cdot CH_2 \cdot CHPhMe$  (?). The latter is a viscous, odourless oil boiling at  $302^\circ$  and having a sp. gr.  $0.9724$  at  $21^\circ/4^\circ$ ; it reduces permanganate slowly and unites with bromine; it is not reduced to isopropylbenzene by sodium and alcohol.

1<sup>1</sup>-Metho-1<sup>1</sup>-propenylbenzene ( $\beta$ -phenyl- $\Delta^{\beta}$ -butylene),  $CPhMe \cdot CHMe$ , is prepared by mixing ethyl iodide, acetophenone, and magnesium in the presence of ether, heating for 5 hours after distilling off the ether, and then decomposing the crystalline mass with dilute sulphuric acid. It is an oil with a pleasant odour boiling at  $191-193^\circ$  and has a sp. gr.  $0.9221$  at  $15^\circ/4^\circ$ ; it forms an oily dibromide; it is oxidised by permanganate to acetophenone and reduced by sodium and alcohol to secondary butylbenzene (b. p.  $172-173^\circ$ ).

1<sup>1</sup>-Metho-1<sup>1</sup>-propenyl-p-iodobenzene ( $\beta$ -p-iodophenyl- $\Delta^{\beta}$ -butylene),



is prepared in a similar manner from p-iodoacetophenone; it is an oil with a pleasant odour, boiling at  $155^\circ$  under 23 mm. pressure, and crystallising in colourless leaflets which melt at  $45-46^\circ$ ; it is oxidised to p-iodoacetophenone and is reduced to a mixture of p-iodo-sec.butylbenzene and sec.butylbenzene.

1<sup>1</sup>-Metho-1<sup>1</sup>-butenylbenzene ( $\beta$ -phenyl- $\Delta^{\beta}$ -amylene),  $\text{CPhMe}\cdot\text{CHEt}$ , is prepared from propyl iodide and acetophenone; the first product of the reaction is *phenylmethylpropylcarbinol*,  $\text{OH}\cdot\text{CPhMePr}$ , an oil boiling at 112—113° under 12 mm., at 116—117° under 16 mm., and at 216° under the ordinary pressure, and having a sp. gr. 0.9723 at 21.5°/4°. The *chloro*-derivative,  $\text{CClPhMe}\cdot\text{CH}_2\text{Et}$ , prepared by the action of hydrogen chloride at 0° on the carbinol, is an unstable oil, which, when boiled with pyridine, is converted into the hydrocarbon; the latter is a colourless, limpid oil, which boils at 89—90° under 16 mm. and at 199° under the ordinary pressure, and has a sp. gr. 0.8976 at 21.2°/4°; it is oxidised to acetophenone and reduced to a *sec.amylbenzene*,  $\text{C}_6\text{H}_5\cdot\text{C}_5\text{H}_{11}$ , which boils at 191°.

1<sup>1</sup>:1<sup>4</sup>-Dimetho-1<sup>1</sup>-pentenylbenzene ( $\beta$ -phenyl- $\Delta^{\beta}$ -isoheptylene),  
 $\text{CPhMe}\cdot\text{CH}\cdot\text{CH}_2\text{Pr}^{\beta}$ ,

obtained from *isoamyl* iodide and acetophenone, is an oily liquid boiling at 121° under 20 mm. pressure and having a sp. gr. 0.8814 at 15°/4°; it is oxidised to acetophenone and valeric acid and reduced to an *isoheptylbenzene*,  $\text{CHPhMe}\cdot\text{CH}_2\cdot\text{CH}_2\text{Pr}^{\beta}$ , which boils at 223° and has a sp. gr. 0.8696 at 15°/4°.

6<sup>1</sup>-Metho-6<sup>1</sup>-propenyl-1:3:4-trimethylbenzene ( $\beta$ - $\psi$ -cumyl- $\Delta^{\beta}$ -butylene),  $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CMe}\cdot\text{CHMe}$ , prepared from aceto- $\psi$ -cumene and ethyl iodide, is a colourless oil boiling at 234—236° and having a sp. gr. 0.8992 at 15°/4°; it is not easily attacked by permanganate. K. J. P. O.

**Synthesis of Arylated Ethylenes.** By AUGUST KLAGES (*Ber.*, 1902, 35, 2646—2649. Compare Abstr., 1899, i, 598).—Diphenylmethylcarbinol,  $\text{CPh}_2\text{Me}\cdot\text{OH}$ , is easily prepared by treating a benzene solution of benzophenone with magnesium and a solution of methyl iodide in ether, and acting on the crystalline mass which is thus formed with ice-cold dilute sulphuric acid; it crystallises in prisms melting at 81°. If the mixture just mentioned is heated for some time at 100°, *as*-diphenylethylene is also produced; the unsaturated hydrocarbon can be obtained from the carbinol by first converting it into the chloride by means of hydrogen chloride and then boiling the latter with pyridine. When *as*-diphenylethylene is reduced with sodium and alcohol, *as*-diphenylethane is formed as a colourless oil boiling at 148° under 22 mm. pressure and having a sp. gr. 0.9877 at 25°/4°; prepared by this method, the hydrocarbon does not exhibit a blue fluorescence. *s*-Diphenylethylene is also very easily reducible to the corresponding ethane, dibenzyl, by the same reagent.

*aa*-Diphenylpropylene,  $\text{CPh}_2\cdot\text{CHMe}$ , prepared in a similar manner from benzophenone and ethyl iodide, forms colourless crystals melting at 52° and boiling at 169—170° under 28 mm. pressure; it is reduced by sodium and alcohol to *diphenylpropane*,  $\text{CPh}_2\cdot\text{CH}_2\text{Me}$ , which is a colourless oil boiling at 153—154° at 20 mm. pressure and has a sp. gr. 0.9751 at 23°/4°.

*a* $\beta$ -Diphenylpropylene,  $\text{CHPh}\cdot\text{CPhMe}$ , is prepared from deoxybenzoin and methyl iodide in the presence of magnesium; it crystallises in plates or leaflets melting at 82—83° and boiling at 183° under 26 mm. pressure. When oxidised by permanganate, only benzoic acid was formed; with chromic acid, on the other hand, acetophenone and benzoic

acid are produced. On reduction, the corresponding diphenylpropane is obtained as an oil which boils at 166—167° under 28 mm. pressure and has a sp. gr. 0.9824 at 23°/4°.

K. J. P. O.

**Phenylbutadiene.** By AUGUST KLAGES (*Ber.*, 1902, 35, 2649—2652).—*Methylstyrylcarbinol*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CHMe}\cdot\text{OH}$ , is prepared from cinnamaldehyde, methyl iodide, and magnesium; the crystalline double compound first formed is decomposed by water; the carbinol is a viscous oil boiling at 144° under 21 mm. pressure, and has a sp. gr. 1.0134 at 22°/4°. The *phenylurethane*,  $\text{C}_{17}\text{H}_{17}\text{O}_2\text{N}$ , obtained from the carbinol and phenylcarbimide, crystallises in needles melting at 94—95°. The *chloride*,  $\text{ChPh}\cdot\text{CH}\cdot\text{CHClMe}$ , prepared by the action of hydrogen chloride on an ethereal solution of the carbinol, is a pale yellow, unstable oil.

*α-Phenylbutadiene*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2$ , obtained by boiling the chloride with pyridine, is a colourless oil boiling at 94—96° under 18 mm. pressure; it is oxidised by the air to a colourless balsam, and polymerises on attempting to distil it under the ordinary pressure. The compound obtained by Doebner (this vol., i, 598) by the dry distillation of cinnamylacrylic acid with barium hydroxide is, therefore, not phenylbutadiene, whereas the compound prepared by Liebermann and Riiber (*Abstr.*, 1900, i, 648) by distilling *allocinnamylideneacetic acid* in a vacuum is this hydrocarbon.

The *tetrabromide* of phenylbutadiene,  $\text{CHPhBr}\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$ , forms colourless leaflets melting at 146°. On reducing the hydrocarbon with sodium and alcohol, *α-phenyl-Δ<sup>β</sup>-butylene*,  $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CHMe}$ , is obtained; its *dibromide* is an oil.

*α-Phenyl-γ-methyl-Δ<sup>αγ</sup>-butadiene*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}_2$ , was prepared by treating benzylideneacetone with magnesium and methyl iodide in ethereal solution, and then adding dilute sulphuric acid to the clear liquid; in this case, the hydrocarbon was obtained directly without the intermediate formation of the carbinol. It is an oil boiling at 124° under 32 mm. pressure, and has a sp. gr. 0.9423 at 23°/4°; on reduction, a dihydro-product, probably *amenylbenzene*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2$ , is formed; it is an oil boiling at 205° and forms a *dibromide*,  $\text{C}_{11}\text{H}_{14}\text{Br}_2$ , which crystallises in leaflets melting at 65—66°.

*α-Phenyl-γ-methyl-Δ<sup>αγ</sup>-pentadiene*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CHMe}$ , prepared from benzylideneacetone and ethyl iodide by a similar method, is a colourless oil with an odour of turpentine; it boils at 132—133° under 21 mm. pressure and has a sp. gr. 0.9523 at 23°/4°; it is oxidised by the air.

K. J. P. O.

*alloPhenylbutadiene.* By CARL LIEBERMANN and C. N. RIIBER (*Ber.*, 1902, 35, 2696—2698).—When cinnamylidenemalonic acid is heated at 180° with quinoline, the *allocinnamylideneacetic acid*, which is first formed (see *Abstr.*, 1895, i, 470), is converted into *allophenylbutadiene*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2$ ; this melts at 4.5°, boils at 95° under 20 mm. pressure, and has a sp. gr. 0.9286 at 20°/4°, and an odour like that of styrene. When heated at 250°, it polymerises to *bisdiphenylbutadiene*,  $\text{C}_{20}\text{H}_{20}$ , which is a thick, viscous oil boiling at 221° under 17 mm. pressure, and has a sp. gr. 1.0325 at 28°/4°, and  $n_D$  1.6016 at 20°.

*allo*Phenylbutadiene differs from the phenylbutadiene described by Doebner (this vol., i, 598) as it combines with 2 mols. of bromine (compare Klages, preceding abstract). R. H. P.

**Ring Formation by means of Magnesium Organic Compounds. A complete Synthesis of Methylcyclopentane.** By NICOLAI ZELINSKY and A. MOSER (*Ber.*, 1902, 35, 2684—2686).—*δ*-Acetylbutyl iodide,  $\text{CH}_2\text{Ac}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{I}$ , prepared from the corresponding alcohol, forms an almost colourless liquid which boils at  $117^\circ$  under 14 mm. pressure and has a sp. gr. 1.5838 at  $23^\circ/4^\circ$ . It readily reacts with metallic magnesium, yielding an additive product which, when decomposed by dilute acetic acid, yields 1-methyl-1-cyclopentanol. It seems probable that the additive compound  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{MgI}$  passes into the form  $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ | \quad | \\ \text{CH}_2\cdot\text{CH}_2 \end{array} > \text{CMe}\cdot\text{O}\cdot\text{MgI}$ , and that this yields with water the alcohol  $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ | \quad | \\ \text{CH}_2\cdot\text{CH}_2 \end{array} > \text{CMe}\cdot\text{OH}$ .

The reaction does not occur with metallic zinc. The alcohol can readily be converted into the iodide, and this, by reduction with zinc dust in presence of acetic acid saturated with hydriodic acid, into the corresponding hydrocarbon, methylcyclopentane, boiling at  $72\text{--}72.2^\circ$  (corr.). A. H.

**Influence of Alkyl Groups on the Activity of Halogenised Benzenes.** By AUGUST KLAGES and W. STORP (*J. pr. Chem.*, 1902, [ii], 65, 564—578. Compare Abstr., 1901, i, 387).—The elimination of halogen from the benzene nucleus is favoured by the presence of methyl in the ortho-, diortho-, or ortho-para-positions, but made more difficult by the presence of a homologue of methyl. The elimination of iodine by treatment with red phosphorus and hydriodic acid is effected with *p*-iodotoluene in two hours at  $182^\circ$ ; with *p*-iodoethylbenzene in five hours at  $218^\circ$ ; *p*-iodoisobutylbenzene and *p*-iodo-*tert*-butylbenzene are unchanged in five hours at  $218^\circ$ ; and iodocetylbenzene does not undergo the reaction at  $230^\circ$ .

The introduction of iodine into the benzene nucleus is similarly effected. When boiled with iodine and iodic acid in glacial acetic acid solution, benzene is not attacked, toluene reacts slowly, ethylbenzene and isobutylbenzene are easily iodinated, but cetylbenzene reacts very slowly. Mesitylene, *s*-dimethylethylbenzene, and *s*-triethylbenzene react easily, but *s*-triphenylbenzene is only slightly attacked after three hours' boiling.

The following new compounds are described:

*p*-Iodoethylbenzene is a colourless oil, boils at  $112^\circ$  under 20 mm. pressure, has a sp. gr. 1.65 at  $14^\circ$ , and forms an iododichloride,  $\text{C}_8\text{H}_9\text{ICl}_2$ , as a yellow, crystalline mass melting at  $90^\circ$ . *p*-Iodoisobutylbenzene is a colourless oil, boils at  $120\text{--}121^\circ$  under 11 mm. pressure, and has a sp. gr. 1.44 at  $11^\circ$ .

*p*-Iodocetylbenzene crystallises in colourless leaflets, melts at  $38^\circ$ , and forms an iododichloride,  $\text{C}_{22}\text{H}_{37}\text{ICl}_2$ , as a yellowish-green, crystalline mass which melts and decomposes at  $86^\circ$ . 2-Iodocymene, prepared



from 2-cymidine, is a colourless oil, boils at  $139^{\circ}$  under 23 mm. pressure, and has a sp. gr. 1.46 at  $14^{\circ}$ . The *iododichloride*,  $C_{10}H_{13}ICl_2$ , forms yellow crystals and melts and decomposes at  $92.5^{\circ}$ . 3-*Iodocymene*, formed by the action of iodine and iodic acid on cymene, is a colourless oil, boils at  $122-124^{\circ}$  under 13 mm. pressure, and has a sp. gr. 1.52 at  $13^{\circ}$ . The *iododichloride* melts at  $87^{\circ}$ , and is easily soluble in chloroform, but more sparingly so in carbon tetrachloride. 2-*Iodo-1-methyl-3-tert.-butyl benzene*, prepared from the amine, is a colourless oil, boils at  $132-133^{\circ}$  under 13 mm. pressure, and has a sp. gr. 1.46 at  $13^{\circ}$ .

*Iododimethylethylbenzene* [ $I:Me_2:Et = 2:1:3:5$ ], formed from *s*-dimethylethylbenzene, is a colourless oil, boils at  $142-144^{\circ}$  under 22 mm. pressure, and has a sp. gr. 1.54 at  $13^{\circ}$ . *Iodocetylmesitylene* melts at  $44^{\circ}$ . G. Y.

**Reduction of Aromatic Nitro-compounds with Tin and Hydrochloric Acid.** By JOHANNES PINNOW (*J. pr. Chem.*, 1902, [ii], 65, 579—585. Compare Abstr., 1901, i, 485).—Experimental proof is given that the addition of graphite accelerates the reduction of nitro-compounds with tin and hydrochloric acid. As in the reduction of nitrodimethyltoluidine under these conditions, 1:5-dimethylbenziminazole is not formed, the nitroso-compound cannot be an intermediate stage in the process (compare Haber, Abstr., 1900, i, 592). 1:5-Dimethylbenziminazole is formed in small quantity when the reduction is electrolytic, the yield being greater with a carbon than with a platinum cathode; when the reduction is retarded by introduction of a resistance, the proportion of the benziminazole formed remains unchanged, but the proportion of chloro-compounds is increased.

G. Y.

**Combination of Alcohol with Nitro-derivatives of Styrene.** By BERNHARD FLÜRSCHHEIM (*J. pr. Chem.*, 1902, [ii], 66, 16—27).—When *o*-bromostyrene is treated with cold fuming nitric acid, two dinitro-bromostyrenes are obtained in addition to *p*-nitrobenzoic acid. *a*-*p*-Nitrophenyl- $\beta$ -bromonitroethylene separates from alcohol in yellow crystals, melts at  $135-136^{\circ}$ , combines only slowly with bromine, and, when boiled with water, yields *p*-nitrobenzaldehyde, nitrobromomethane, nitric acid, and hydrogen bromide; when boiled with ethyl alcohol, it yields *a*-*p*-nitrophenyl-*a*-ethoxy- $\beta$ -nitrobromoethane, which forms colourless crystals, melts at  $95-96^{\circ}$ , dissolves in caustic alkalis giving yellow solutions, which are decolorised by bromine, giving *a*-*p*-nitrophenyl-*a*-ethoxy- $\beta$ -nitrodibromoethane melting at  $145.5^{\circ}$ . *a*-*o*-Nitrophenyl- $\beta$ -bromonitroethylene crystallises from acetic acid, melts at  $88^{\circ}$ , and is decomposed by water into *o*-nitrobenzaldehyde and bromonitromethane; it is insoluble in alkalis and combines with alcohol far less readily than the *p*-derivative forming the ethoxy-compound, which melts at about  $60^{\circ}$ , and with bromine yields the *a*-*o*-nitrophenyl-*a*-ethoxy- $\beta$ -nitrodibromoethane melting at  $70.5^{\circ}$ . *o*-Nitrostyrene, *p*-*o*-dinitrostyrene, and *o*-bromostyrene do not combine with boiling ethyl alcohol.

The paper concludes with a discussion of the conditions necessary for the addition of ethyl alcohol to an ethylene derivative, and of the formulæ of primary and secondary nitro-compounds. R. H. P.

**9-Aminophenanthrene.** By ROBERT PSCHORR and J. SCHRÖTER (*Ber.*, 1902, **35**, 2726—2729). Compare Schmidt and Strobel, *Abstr.*, 1901, i, 464).—*Ethyl phenanthrene-9-carboxylate* crystallises in needles or flat plates, melts at  $61^{\circ}$ , and is readily soluble in the usual organic solvents. The *hydrazide*,  $C_{14}H_9 \cdot CO \cdot NH \cdot NH_2$ , crystallises from hot water or benzene in colourless needles melting at  $228^{\circ}$  and readily soluble in glacial acetic acid. On treatment with sodium nitrite solution, it is converted into the *azoimide*,  $C_{14}H_9 \cdot CO \cdot N_3$ , melting at  $94^{\circ}$ , and this, when warmed with alcohol, yields 9-phenanthrylurethane.

9-Hydroxyphenanthrene is obtained when the urethane is hydrolysed with concentrated hydrochloric acid and 9-aminophenanthrene when the urethane is heated with concentrated ammonia at  $180^{\circ}$  for two hours.  
J. J. S.

**9-Amino-10-hydroxyphenanthrene, Morphigenin, and 9:10-Diaminophenanthrene.** By ROBERT PSCHORR [with J. SCHRÖTER] (*Ber.*, 1902, **35**, 2729—2740).—Vahlen's morphigenin chloride, 9-amino-10-hydroxyphenanthrene hydrochloride (*Arch. exp. Path. Pharm.*, 1902, **47**, 368), may be obtained by the reduction of phenanthraquinoneimide or of phenanthraquinone monoxime with stannous chloride and hydrochloric acid. When warmed with water or dilute acids, it is converted into phenanthraquinol; nitrous or nitric acid yields phenanthraquinone. The free base may be obtained by the action of alkali sulphite, acetate, or carbonate on the hydrochloride in the absence of air; it forms brownish needles, begins to sinter at  $150^{\circ}$ , and is completely melted at  $417^{\circ}$ . It dissolves in alkali without undergoing decomposition if air is absent. When the alkaline solution is warmed in an atmosphere of hydrogen, the products are ammonia and 9:10-dihydroxyphenanthrene, the *acetyl* derivative of which melts at  $202^{\circ}$ . In the presence of air, the products are the corresponding quinone and quinhydrone.

9-Acetylamino-10-hydroxyphenanthrene crystallises in colourless, flat needles melting at  $223$ — $224^{\circ}$  (corr.), and on further treatment with acetic anhydride yields 9-acetylamino-10-acetoxypheanthrene, which crystallises from acetic acid in six-sided prisms melting at  $242^{\circ}$  (corr.). Benzoyl chloride converts the base into *anhydrobenzoyl-10-hydroxy-9-aminophenanthrene*,  $C_{21}H_{13}ON$ , which crystallises in glistening needles melting at  $205^{\circ}$  (corr.).

10-Hydroxy-9-phenanthrylphenylcarbamide,  $C_{21}H_{16}O_2N_2$ , obtained by the action of phenylcarbimide on the base, crystallises in small needles melting at  $241^{\circ}$  (corr.).

9:10-Diaminophenanthrene, obtained by the reduction of phenanthraquinonedioxime with stannous chloride and concentrated hydrochloric acid, forms yellowish plates melting at  $160$ — $166^{\circ}$  in the crude state. Its *diacetyl* derivative crystallises in six-sided plates melting and decomposing at  $330^{\circ}$  (corr.). The free base readily loses ammonia and yields diphenanthryleneazotide (Japp, *Trans.*, 1886, **49**, 843).

J. J. S.

**Synthesis of 1-Methyl-1-cyclopentanol.** By NICOLAI ZELINSKY and S. NAMJETKIN (*Ber.*, 1902, **35**, 2683).—*cyclopentanone*, prepared from adipic acid, yields a complex product with magnesium and methyl

iodide in presence of ether, and this is decomposed by water with formation of 1-methyl-1-cyclopentanol,  $\text{CH}_2 \begin{matrix} \text{CH}_2 \cdot \text{CMe} \cdot \text{OH} \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{matrix}$ , which boils at  $135^\circ$  under 737 mm. pressure and sublimates in thin needles melting at  $35-37^\circ$ . A. H.

**A New Di-iodophenol.** By P. BRENANS (*Compt. rend.*, 1902, 135, 177—179. Compare *Abstr.*, 1901, i, 322, 643; and this vol., i, 280).—4-Iodo-o-nitroaniline was prepared by the action of 1 mol. of iodine chloride on 1 mol. of o-nitroaniline in acetic acid solution. It is isolated by distillation in steam; it separates from hot water in orange needles and melts at  $122^\circ$ .

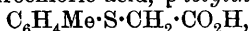
By dissolving this substance in a mixture of acetic and sulphuric acids, and, after cooling, adding sodium nitrite, then pouring in a solution of potassium iodide, 3:6-di-iodonitrobenzene is formed; this crystallises from hot water in slender, yellow needles, melts at  $109-110^\circ$ , and is soluble in alcohol, ether, chloroform, or benzene.

When this nitro-compound is reduced in acid solution with stannous chloride, 3:6-di-iodoaniline is obtained, which crystallises from hot water in colourless needles, has an odour recalling that of naphthalene, and melts at  $88-89^\circ$ . It is volatile with steam and soluble in the ordinary organic solvents. Its solutions become coloured on exposure to light.

When diazotised in presence of acetic acid and sulphuric acid and then distilled in steam, the di-iodoaniline gives colourless needles of 3:6-di-iodophenol. This crystallises from light petroleum, melts at  $99^\circ$ , is slightly soluble in water or ether, and readily so in alcohol, acetic acid, or benzene. Its acetate,  $\text{C}_2\text{H}_3\text{O}_2 \cdot \text{C}_6\text{H}_3\text{I}_2$  [1:3:6], forms elongated, colourless prisms, melts at  $70^\circ$ , and is very soluble in acetic acid, methyl alcohol, or benzene. J. McC.

**Some Derivatives of the Thiocresols.** By CH. RABAUT (*Bull. Soc. Chim.*, 1902, [iii], 27, 690—692).—p-Tolyl thiocyanate, obtained from p-toluidine by the Sandmeyer reaction, forms a clear yellow liquid which boils without appreciable decomposition at  $240-245^\circ$  under the ordinary pressure, and at  $155-158^\circ$  under 40—50 mm. pressure; it is insoluble in water, but soluble in alcohol, benzene, chloroform, or glacial acetic acid. It does not combine with cuprous chloride. When treated with an aqueous or alcoholic solution of potassium hydroxide, p-tolyl disulphide,  $\text{S}_2(\text{C}_6\text{H}_4\text{Me})_2$ , is obtained in the form of white crystals melting at  $45^\circ$ . p-Tolyl thiocyanate, treated with an alcoholic solution of potassium hydrogen sulphide, yields thio-p-cresol. This gives, with lead acetate, a precipitate,  $(\text{C}_6\text{H}_4\text{Me} \cdot \text{S})_2\text{Pb}$ , which, when treated with bromine, gives p-tolyl disulphide, and with acetyl chloride the acetate of p-tolyl thioacetate,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{S} \cdot \text{Ac}$ ; the latter is a colourless liquid which boils without decomposition at  $240-243^\circ$  under 760 mm. pressure. The benzoyl ester,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{S} \cdot \text{SBz}$ , obtained in a similar manner, forms white needles melting at  $75^\circ$ .

On heating a mixture of p-tolyl thiocyanate and chloroacetic acid in molecular proportion, saponifying the product with sodium hydroxide, and acidifying with hydrochloric acid, p-tolylthioglycollic acid,



is obtained in white crystals melting at  $90^{\circ}$ . It is very sparingly soluble in cold water, fairly so in boiling water, and very soluble in the usual solvents and in acetic acid. It can be synthesised by heating *p*-thiocresol with chloroacetic acid, and on oxidation with chromic acid yields *p*-sulphobenzoic acid. The corresponding *o*-tolylthioglycollic acid, melting at  $106^{\circ}$ , can be obtained by the action of chloroacetic acid on *o*-tolyl thiocyanate or on *o*-thiocresol. It has the same general properties as the para-compound.

A. F.

**Esters derived from 2:3-Methoxynaphthol.** By RUD. ENGELHARDT (*J. pr. Chem.*, 1902, [ii], 65, 536).—2:3-Methoxynaphthol melts at  $109^{\circ}$ . It forms a *benzoate*, which crystallises from alcohol in white leaflets and melts at  $133^{\circ}$ , a *salicylate* which crystallises in delicate needles and melts at  $138^{\circ}$ , a *valerate* which crystallises in white, soft leaflets and melts at  $76^{\circ}$ , an *acetate* which crystallises from glacial acetic acid in needles and melts at  $117^{\circ}$ , and a *phosphate* which melts above  $275^{\circ}$ . The action of phosgene on 2:3-methoxynaphthol in aqueous solution leads to the formation of two *substances*, the one of which melts at  $82^{\circ}$ , and is easily soluble in alcohol, the other melts at  $186^{\circ}$ , and is sparingly soluble in alcohol, but easily so in hot benzene or chloroform; on hydrolysis, both give the 2:3-methoxynaphthol. G Y.

**Action of Iodine on Catechol in Pyridine Solution.** By GIOVANNI ORTOLEVA (*Gazzetta*, 1902, i, 32, 447—452).—To explain the action of iodine on quinol in pyridine solution, the author and di Stefano (this vol., i, 54) found it necessary to assume that the quinol is first converted into quinone by the oxidising action of the iodine. This assumption is now confirmed by the author's observation that resorcinol is not acted on by iodine in pyridine solution, whilst catechol, which forms *o*-benzoquinone on oxidation, gives a compound similar to that yielded by quinol.

The additive compound of *o*-benzoquinone and pyridine hydriodide,  $C_6H_4O_2 \cdot C_5H_5N \cdot HI$ , crystallises from dilute alcohol in short, yellow needles melting at  $243$ — $245^{\circ}$ , and from water in yellow scales, which contain  $1H_2O$  and darken at  $250^{\circ}$ , but are still unfused at  $263^{\circ}$ . The *acetyl* derivative,  $C_{11}H_9O_2NIAc$ , is deposited from water or alcohol in yellow plates which melt at  $205$ — $207^{\circ}$  and are soluble in alkalis, giving a blood-red solution.

T. H. P.

**A Methylcyclohexanose.** By NICOLAI ZELINSKY and M. ROSCHDESTWENSKY (*Ber.*, 1902, 35, 2695—2696).—1-Methyl-3-cyclohexanone is converted by bromine into a *bromo*-compound,  $C_7H_{11}OBr$ , which boils at  $106$ — $107^{\circ}$  under 13 mm. pressure, melts at  $83$ — $85^{\circ}$ , and has  $[a]_D - 47.9^{\circ}$ . A liquid product, which boils at a somewhat lower temperature and attacks the eyes violently, is also formed. The solid *bromo*-compound is converted by concentrated aqueous potash into a *keto*-alcohol, *methylcyclohexanose*,  $C_7H_{13}O_2$ , the exact constitution of which has not been decided. This substance boils at  $85$ — $86^{\circ}$  under 12 mm. pressure, has a sp. gr. 1.0399 at  $19^{\circ}/4$ ,  $n$  1.4657 at  $19^{\circ}$ , and  $[a]_D 21.6^{\circ}$ . It reduces Fehling's solution and silver nitrate in the cold, and yields a characteristic reddish-violet coloration with ferric

chloride. This substance is of simpler constitution than the cyclic ketotriose of Harries (this vol., i, 378). A. H.

**Characterisation of Pseudoacids by the Ammonia Reaction.** By ARTHUR HANTZSCH and E. DOLLFUS (*Ber.*, 1902, 35, 2724—2725. See this vol., i, 223).—A constant error in the calculations is noted, but it does not alter the conclusions reached in the earlier paper.

R. H. P.

**A Direct Synthesis of Hexahydroaromatic Acids and Polymethylenecarboxylic Acids in General.** By NICOLAI ZELINSKY (*Ber.*, 1902, 35, 2687—2692).—The iodine and bromine derivatives of *cyclohexane* and its homologues react with metallic magnesium to form organometallic compounds which, with carbon dioxide, yield the magnesium salts of the corresponding carboxylic acids (compare Grignard, *Abstr.*, 1901, i, 679).

By this reaction, *iodocyclohexane* is converted into *cyclohexanecarboxylic acid* (hexahydrobenzoic acid); and 3-iodo-1-methyl*cyclohexane* yields 1-methyl*cyclohexane*-3-carboxylic acid (hexahydro-*m*-toluic acid), which boils at 134° under 15 mm. pressure.

1:3-Dimethyl-5-cyclohexanecarboxylic acid,  $C_6H_9Me_2 \cdot CO_2H$  (hexahydro-*m*-xylic acid), may be prepared from 5-iodo-1:3-dimethyl*cyclohexane*, and boils at 139° under 15 mm. pressure. It has a sp. gr. 0.9785 at 20°/4°,  $n_D^{14} 1.4577$  at 20°, and yields an *amide* melting at 153.5—154.5°.

1-Methylcyclopentane-3-carboxylic acid,  $\begin{array}{c} CHMe \cdot CH_2 \\ | \\ CH_2 - CH_2 \end{array} > CH \cdot CO_2H$ , is prepared from the corresponding iodide and boils at 115—116° under 15 mm. pressure. The acid has a sp. gr. 1.006 at 22°/4°,  $n_D^{14} 1.4480$  at 22° [ $\alpha_D$ ] — 5.89°. The *chloride* boils at 173—175°, and the *amide* crystallises in lustrous prisms melting at 149—150°. This acid may possibly be identical with the  $\beta$ -methylpentamethylenecarboxylic acid of Euler (*Abstr.*, 1895, i, 145). Finally, *cycloheptanecarboxylic acid* can readily be obtained in a similar manner from the *bromide* prepared from suberol, which boils at 75° under 12 mm. pressure and has a sp. gr. 1.2887 at 22°/4°, and  $n_D^{14} 1.4996$  at 22°. A. H.

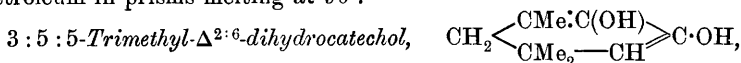
**Syntheses of Benzoic Acid and Phenylacetic Acid as Lecture Experiments.** By NICOLAI ZELINSKY (*Ber.*, 1902, 35, 2692—2694).—Benzoic acid can be readily and rapidly synthesised by the action of a stream of dry carbon dioxide on an ethereal solution of magnesium phenyl iodide, which is prepared by the action of magnesium on iodo-benzene in presence of dry ether. The complex magnesium compound separates as an oil which is decomposed by water with formation of magnesium benzoate. The acid is liberated by sulphuric acid, extracted with ether, and the ethereal solution washed with a few drops of sodium thiosulphate solution and evaporated, pure benzoic acid being obtained.

A similar reaction may be carried out with magnesium benzyl chloride, an ethereal solution of which yields, with a current of dry carbon dioxide, crystals of the formula  $CH_2Ph \cdot CO_2MgCl, C_4H_{10}O$ . These are decomposed by water with formation of a salt of phenylacetic acid, from which the pure acid can be readily obtained. The zinc organo-metallic

compounds, such as zinc ethyl iodide, appear to undergo no reaction with carbon dioxide. A. H.

**Action of Formaldehyde on Methyl Anthranilate.** By HANS MEHNER (*J. pr. Chem.*, 1902, [ii], 65, 533—536. Compare Abstr., 1901, i, 470, and Erdmann, Abstr., 1901, i, 536).—The author has confirmed his previous work and is unable to obtain Erdmann's results. G. Y.

**Condensation Products of Tetronic Acid.** By LUDWIG WOLFF [with MAX GABLER and FRITZ HEYL] (*Annalen*, 1902, 322, 351—391. Compare Abstr., 1901, i, 283).—The *benzoyl* derivative of ketohexyltetronic acid, prepared by treating the sodium salt with benzoyl chloride and sodium carbonate, crystallises from chloroform and light petroleum in prisms melting at 96°.



obtained by heating ketohexyltetronic acid with dilute hydrochloric acid for 2 hours at 120°, crystallises from dilute alcohol or ether in white, felted needles, melts at 91—92°, and sublimes without decomposition; it is neutral to litmus and gives a dark violet coloration with ferric chloride. The *dioxime*,  $\text{C}_9\text{H}_{16}\text{O}_2\text{N}_2$ , crystallises from dilute alcohol in needles melting at 166°; it is insoluble in sodium carbonate, but dissolves in sodium hydroxide solution or concentrated hydrochloric acid and gives a brownish-red ferric chloride coloration.

2:4:4-Trimethyl-N-hydroxy- $\Delta^{2:5}$ -dihydroquinolide, the *pseudo-oxime* of ketohexyltetronic acid,  $\begin{array}{c} \text{CMe}\cdot\text{N(OH)}\cdot\text{C}\cdot\text{CH}_2 \\ | \quad | \\ \text{CH—CMe}_2\text{—C—CO} \end{array} \text{O}$ , results from the interaction of ketohexyltetronic acid and hydroxylamine hydrochloride in aqueous solution; it is sparingly soluble in concentrated hydrochloric acid and the ordinary solvents, crystallises from boiling alcohol and acetone in stellar aggregates of long plates, becomes yellow at 200° and decomposes at 210°; when rapidly heated, the decomposition takes place at 212—216°.

2:3:4-Trimethylquinolide,  $\begin{array}{c} \text{CMe}\cdot\text{N—C}\cdot\text{CH}_2 \\ | \quad | \\ \text{CMe}\cdot\text{CMe}\cdot\text{C—CO} \end{array} \text{O}$ , produced by treating the oxime of acetonylpropylidenebistetrionic acid with glacial acetic acid, crystallises in long needles melting at 152°; it has a neutral reaction and does not interact with acetic anhydride or nitrous acid; its *picrate*,  $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OH}$ , separates, on mixing alcoholic solutions of its generators, in yellow needles sintering at 160° and melting at 169°; the *hydrochloride* is readily soluble in water and separates from alcoholic solutions in prisms decomposing at 220°; it is dissociated by water and ether. The *platinichloride*,  $(\text{C}_{10}\text{H}_{11}\text{O}_2\text{N})_2\cdot\text{H}_2\text{PtCl}_6\cdot 2\text{H}_2\text{O}$ , crystallises in reddish-yellow prisms.

The base is stable towards cold alkali solutions, but, on warming, hydrolysis occurs, and by the use of barium hydroxide the *barium* salt of 2:3:4-trimethyl-6-hydroxymethylquinolinic acid is produced, this substance separating from water in nodular aggregates; the *silver* salt,  $\text{C}_{10}\text{H}_{12}\text{O}_3\text{NAg}$ , crystallises in sparingly soluble needles; the free *acid*,

obtained by adding sulphuric acid to a solution of the barium salt, crystallises in colourless prisms and melts at  $169^{\circ}$ , becoming reconverted into the original lactone base; this change is also slowly induced by boiling with water or dilute hydrochloric acid.

2:3:4-Trimethylquinolide methiodide,  $\begin{array}{c} \text{CMe} \cdot \text{NMeI} \cdot \text{C} \cdot \text{CH}_2 \\ | \quad | \\ \text{CMe} \cdot \text{CMe} - \text{C} - \text{CO} \end{array} > \text{O}$ , prepared by heating its generators at  $100^{\circ}$ , crystallises from hot water in yellow prisms melting at  $116$ — $120^{\circ}$ ; at higher temperatures, it dissociates into its generators; the *platinichloride*,  $(\text{C}_{11}\text{H}_{13}\text{O}_2\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$ , produced by treating the iodide successively with silver chloride and platinic chloride, crystallises from hydrochloric acid in prisms exhibiting cruciform twinning and melting at  $225^{\circ}$ .

The *pseudo-ammonium base*,  $\begin{array}{c} \text{CMe} \cdot \text{NMe} - \text{C} \cdot \text{CH}_2 \\ | \quad | \\ \text{CMe} \cdot \text{CMe}(\text{OH}) - \text{C} - \text{CO} \end{array} > \text{O}$  or  $\begin{array}{c} \text{OH} \cdot \text{CMe} \cdot \text{NMe} - \text{C} \cdot \text{CH}_2 \\ | \quad | \\ \text{CMe} \cdot \text{CMe} - \text{C} - \text{CO} \end{array} > \text{O}$ ,

is the final product of the action of alkali hydroxides or carbonates on the preceding iodide; when, however, the reaction is performed by means of moist silver oxide, there is evidence that an intermediate compound is formed having the alkaline properties of a true ammonium hydroxide. The pseudo-base crystallises from water in colourless, monoclinic plates containing  $3\text{H}_2\text{O}$ ; it becomes anhydrous at  $100^{\circ}$ , changes colour to yellow at  $230^{\circ}$  and decomposes at  $259^{\circ}$ . This compound does not react with hydroxylamine or phenylhydrazine; methyl iodide or hydrochloric acid converts it into the corresponding salt of the true ammonium derivative.

2:3:4-Trimethylquinolinic acid,  $\begin{array}{c} \text{CMe} \cdot \text{N} - \text{C} \cdot \text{CO}_2\text{H} \\ | \quad | \\ \text{CMe} \cdot \text{CMe} - \text{C} \cdot \text{CO}_2\text{H} \end{array}$ , obtained by oxidising 2:3:4-trimethyl-6-hydroxymethylquinolinic acid with an alkaline solution of potassium permanganate, crystallises from water or alcohol in prisms, and melts at  $194$ — $195^{\circ}$  with evolution of carbon dioxide; at higher temperatures it again becomes solid and finally boils at  $250^{\circ}$ . The *silver* salt is a gelatinous precipitate, the *lead* salt crystallises in needles or prisms.

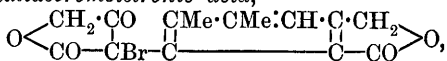
2:3:4-Trimethylnicotinic acid,  $\text{C}_5\text{NHMe}_3 \cdot \text{CO}_2\text{H}$ , produced by heating the preceding acid at  $160$ — $170^{\circ}$ , crystallises from alcohol in prisms melting at  $257^{\circ}$ ; its carboxyl group is probably situated in the *m*-position with respect to the nitrogen, but this is not known with certainty.

2:4-Dimethylpyridine-3:5:6-tricarboxylic acid, prepared by oxidising the dicarboxylic acid with hot permanganate solution, melts at  $218^{\circ}$  and is identical with the product obtained by Hantzsch from lutidinetricarboxylic acid; when heated with water at  $170^{\circ}$ , it loses one carboxyl group and becomes converted into 2:4-dimethylpyridine-3:5-dicarboxylic acid. Further oxidation of the tricarboxylic acid leads to the production of  $\gamma$ -picolinetetracarboxylic acid and pyridine-pentacarboxylic acid; these compounds, when heated with glacial acetic acid at  $130^{\circ}$ , lose the two carboxyl groups in the ortho-position with respect to the nitrogen atom, yielding  $\gamma$ -picoline-3:5-dicarboxylic acid and pyridine-3:4:5-tricarboxylic acid respectively.

*iso*Acetophoroneoxime, dimethylcyclohexenoneoxime, and methylcyclohexenoneoxime, when heated with hydrochloric acid, lose the elements of water and become converted into 5-amino-1 : 2 : 3-trimethylbenzene, *s*-xylidine, and *m*-toluidine respectively, this transformation being in each case accompanied by a shifting of one methyl group from the complex  $>CMe_2$  to an adjacent carbon atom of the nucleus.

*Dimethylphthalidetetronic acid*,  $O\langle\begin{smallmatrix} CH_2 \\ CO \end{smallmatrix}\rangle C_6HMe_2 \cdot C_4H_3O_3$ , produced from dimethyldihydrophthalidetetronic acid (see Abstr., 1901, i, 285) by warming with concentrated sulphuric acid containing 1—2 per cent. of sulphur trioxide, is a monobasic acid crystallising from boiling alcohol or water in aggregates of needles and melting at  $289^\circ$ ; it develops with ferric chloride a cherry-red coloration.

*Dimethylphthalidebromotetronic acid*,



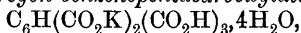
obtained by treating the preceding substance with bromine in the presence of water, crystallises from chloroform and petroleum in colourless prisms or plates and decomposes at  $178$ — $179^\circ$ ; when heated with dilute hydrochloric acid or alcohol, it gives rise to the original compound.

*Dimethylphthalideacetic acid*,  $O\langle\begin{smallmatrix} CH_2 \\ CO \end{smallmatrix}\rangle C_6HMe_2 \cdot CH_2 \cdot CO_2H$ , results from the potash fusion of dimethylphthalidetetronic acid and crystallises from dilute alcohol in white needles melting at  $212$ — $214^\circ$ ; both these substances are monobasic acids.

*Dimethylhomophthalcarboxylic acid*, produced from the preceding compound by first hydrolysing the lactone rings with concentrated potassium hydroxide solution and then oxidising the product with cold potassium permanganate solution, crystallises from hot water in short prisms containing  $2H_2O$  and melting at  $218$ — $220^\circ$ ; the anhydrous acid melts at  $221^\circ$ . When titrated with phenolphthalein, the substance behaves as a tribasic acid; it yields sparingly soluble lead and *silver* salts, the latter having the composition  $C_{12}H_{10}O_6Ag_2$ .

*Benzenepentacarboxylic acid*, produced when the preceding oxidation is carried out with excess of the reagent, crystallises from hot water in needles containing  $5H_2O$  and melting at  $238^\circ$ . A compound said to have the same composition was described by Friedel and Crafts as an amorphous substance containing  $6H_2O$ . The crystalline acid has, however, all the required properties; its neutral potassium salt, on distillation with calcium carbonate, yields a mixture of benzene and diphenyl; the free acid, when heated at  $240$ — $250^\circ$ , furnishes an anhydride and at  $270$ — $300^\circ$  loses carbon dioxide, giving rise to the anhydride of pyromellithic acid.

*Dipotassium trihydrogen benzenepentacarboxylate*,



obtained by adding dilute sulphuric acid to a solution of the normal salt, crystallises in plates. *Potassium tetrahydrogen benzenepentacarboxylate*,  $C_6H(CO_2H)_4 \cdot CO_2K \cdot 2\frac{1}{2}$  or  $3H_2O$ , crystallises in felted, silky needles.

Dimethyldihydrophthalidetetronic acid, when heated with 20 per



cent. hydrochloric acid at  $170^{\circ}$ , loses carbon dioxide and becomes converted into a neutral compound,  $C_{13}H_{14}O_3$ , which crystallises from dilute alcohol in white needles or prisms melting at  $139^{\circ}$ ; this substance gives no ferric chloride coloration, but yields an oxime melting at  $172^{\circ}$  and dissolving in hydrochloric acid or dilute sodium hydroxide solution. The formula  $O \begin{array}{c} \text{CH}_2 \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{CO} \quad \text{C} \end{array}$  is suggested for the intermediate product of this reaction, the substance,  $C_{13}H_{14}O_3$ , actually isolated being an *eso*-anhydride produced by the elimination of 1 mol. of water. G. T. M.

**Aromatic Glutaric Acids.** By SAMUEL AVERY (*Amer. Chem. J.*, 1902, 28, 48—59).—[With H. C. PARMELEE.]— $\beta$ -p-Tolylglutaric acid, obtained by hydrolysing the ester formed by the condensation of ethyl p-tolylacrylate with ethyl sodiomalonate, crystallises from hot water in transparent, oblique prisms, melts at  $165$ — $167^{\circ}$ , and is soluble in ethyl acetate or chloroform. The silver, copper, and calcium salts were prepared and analysed. The anhydride, prepared by heating the acid above its melting point or by treating it with hot acetyl chloride, forms feathery crystals and melts at  $153^{\circ}$ . By the action of aniline on the anhydride,  $\beta$ -p-tolylglutaranilic acid is obtained which crystallises in white needles and melts at  $194$ — $196^{\circ}$ ; its silver salt was analysed. If the anilic acid is heated above its melting point,  $\beta$ -p-glutaranil is produced, which crystallises in long needles and melts at  $174.5^{\circ}$ .

[With M. C. GERE.]— $\beta$ -m-Nitrophenylglutaric acid (Knoevenagel, *Abstr.*, 1899, i, 214) was prepared by hydrolysis of the tricarboxylic ester formed by the action of ethyl sodiomalonate on ethyl m-nitrocinnamate; its silver, calcium, barium, and copper salts were prepared. The anhydride, obtained by the action of boiling acetic anhydride on the acid, forms white, silky crystals and melts at  $170.5^{\circ}$ . The anilic acid melts at  $160^{\circ}$ ; its silver salt was prepared and analysed.

[With HAL. T. BEANS.]—By the action of fuming nitric acid on  $\beta$ -phenylglutaric acid,  $\beta$ -p-nitrophenylglutaric acid is obtained, which crystallises in hard, short prisms, melts at  $237^{\circ}$ , and is soluble in alcohol, ethyl acetate, or glacial acetic acid; a smaller quantity of another substance is simultaneously produced, which forms light yellow crystals, melts at  $175^{\circ}$ , and is probably  $\beta$ -o-nitrophenylglutaric acid. The silver, calcium, and barium salts of the p-acid are described.  $\beta$ -p-Nitrophenylglutaric anhydride, obtained by the action of boiling acetic anhydride on the acid, forms pale yellow crystals, melts at  $122.5^{\circ}$ , and is soluble in ethyl acetate. The dimethyl ester crystallises in large, nearly colourless, plates and melts at  $62^{\circ}$ . The anilic acid crystallises from dilute alcohol in light, glistening flakes and melts at  $120$ — $121^{\circ}$ ; its silver salt was analysed. The anil forms white needles and melts at  $203^{\circ}$ . E. G.

**Chrysodiphenic Acid.** (2-Phenylnaphthalene-1:2'-dicarboxylic Acid). By CARL GRAEBE and R. GNEHM, jun. (*Ber.*, 1902, 35, 2744—2746).—Chrysodiphenic acid (2-phenylnaphthalene-1:2'-dicarboxylic acid),  $CO_2H \cdot C_{10}H_6 \cdot C_6H_4 \cdot CO_2H$ , is formed when Graebe and Hönigsberger's amic acids,  $CO_2H \cdot C_{10}H_6 \cdot C_6H_4 \cdot CO \cdot NH_2$ , and

$\text{NH}_2 \cdot \text{CO} \cdot \text{C}_{10}\text{H}_6 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , are fused with sodium hydroxide for four hours at  $210\text{--}220^\circ$ . It melts at  $199^\circ$  (corr.), and is only sparingly soluble in cold water. Acetic anhydride converts it into an anhydride, and direct esterification yields an acid ester. Concentrated sulphuric acid gives rise to a mixture of two monobasic acids. J. J. S.

**Lichens and their Characteristic Constituents. VII.** By OSWALD HESSE (*J. pr. Chem.*, 1902, [ii], 65, 537—563. Compare Abstr., 1901, i, 595).—*Usnea ceratina* (Ach.), gathered from Java cinchona bark, contains usnaric acid, *d*-usnic acid, parellic acid, and *ceratin*, which forms small, white crystals, melts at  $226^\circ$ , and gives a purple-violet colour with ferric chloride in alcoholic solution.

*Usnea barbata* ( $\alpha$ ) *florida*, from Ceylon cinchona bark, contains *d*-usnic acid, usnaric acid, parellic acid, and usnarin.

*Usnea barbata* ( $\beta$ ) *hirta*, from Ceylon cinchona bark, contains *d*-usnic acid, usnaric acid, barbatic acid, and usnarin.

*Alectoria articulata*, from Java and Jamaica cinchona barks, contains a small proportion of *d*-usnic acid and a trace of usnaric acid.

*Alectoria canariensis*, from Jamaica cinchona bark, contains usnaric acid, *d*-usnic acid ( $[\alpha]_D + 489.1^\circ$  at  $15^\circ$  in chloroform solution).

The formula for usnidic acid is now found to be  $\text{C}_{14}\text{H}_{14}\text{O}_6 \cdot 3\text{H}_2\text{O}$ ; when slowly heated, it begins to melt and decompose at  $187^\circ$ , and at  $192^\circ$  is completely melted to a brown mass; when rapidly heated, it melts at  $195^\circ$ . It is slightly soluble in boiling water, from which it crystallises in delicate needles easily soluble in acetone and hot glacial acetic acid, but only sparingly so in dilute acetic acid. With ferric chloride, the aqueous solution gives no coloration, the alcoholic solution gives an intense ink-blue colour. The *potassium* salt crystallises from hot dilute alcohol in light yellow needles; the *sodium* salt,  $\text{C}_{14}\text{H}_{13}\text{O}_6\text{Na} \cdot 2\text{H}_2\text{O}$ , forms small, yellow needles, soluble in cold water with separation of part of the acid, which dissolves completely in hot water. In presence of a slight excess of alkali, the aqueous solution gradually absorbs oxygen, becoming at first green and finally brown. The *barium* salt crystallises in stellate groups of needles containing  $3\text{H}_2\text{O}$ ; the *silver* salt, obtained as a flocculent, gelatinous precipitate, on addition of silver nitrate to the aqueous solution of the sodium salt, is not changed on boiling, becomes brown on exposure to light, and is easily soluble in aqueous ammonia. When heated in a stream of hydrogen, usnidic acid decomposes into carbon dioxide and *usnidole*,  $\text{C}_{13}\text{H}_{14}\text{O}_4$ , which sublimes in long, yellow needles, melts at  $176^\circ$ , and gives, with ferric chloride, no colour in aqueous solution, but a blue colour in alcoholic solution.

Usnidic acid is identical with the acid obtained from usnic acid by Salkowski (Abstr., 1901, i, 152) and with the pyrousnitic acid and pyrousnic acid of Paternò (Abstr., 1882, 1079).

*Cornicularia aculeata* (Ach.), from the Gerlinger Höhe, between Schloss Solitude and Leonberg (Württemberg), contains rangiformic acid.

*Evernia divaricata*, from Brand (Vorarlberg), contains no usnic acid (compare Abstr., 1898, i, 522, and Zopf, Abstr., 1901, i, 546).

*Evernia prunastri*, from Feuerbach, is found to contain usnic acid, which is not present in two specimens from Teinach (Black Forest).

*Ramalina yemensis*, from *Aspidosperma Quebracho*, Cordoba (Argentine), contains a small proportion of *d*-usnic acid, and an acid crystallising in small, white needles from alcohol, sparingly soluble in ether, and giving a purple-red colour with ferric chloride in alcoholic solution.

*Cladonia alpicornis*, from the Gerlinger Höhe, contains usnic acid (m. p. 196°).

*Cetraria pinastri*, from Liechtenstein, has been re-examined and its composition confirmed. Stietaurin, which, according to Zopf (*loc. cit.*) is contained in *Sticta desfontainii* (*a*) *munda* and in *Sticta aurata*, is a mixture of pulvic anhydride and calycin, both of which are optically inactive (compare Salkowski, *loc. cit.*).

*Parmelia glabra*, from Calmbach, contains lecanoric acid.

The presence of lecanoric acid in *Parmelia sorediata* is confirmed.

*Physcia cæsia*, from Brand (Vorarlberg) and from Liechtenstein, contains atranorin and zeorin, as stated by Zopf, but no hæmatommic acid is present. Zeorin does not react with phenylhydrazine.

*Nephromium lævigatum* (*a*) *genuinum*, from Liechtenstein, contains a small proportion of an acid, which is easily soluble in alcohol and gives a greenish-brown coloration with ferric chloride but no coloration with bleaching powder.

*Placodium circinatum* (*a*) *radiosum*, from Brand, contains salazic acid.

*Placodium gypsaceum*, contains no usnic acid (compare Zopf).

*Callospisma flavovirescens*, from Brand, contains physcion, which melts at 207—208°. Zopf gives m. p. 205°.

*Hæmatomma coccineum* var. *abortivum*, from Teinach (Black Forest), contains coccic acid, atranorin, hæmatommin, and hæmatommidin. Coccic acid,  $C_{12}H_{16}O_{10} \cdot 3H_2O$ , crystallises in delicate, white needles, becomes brown at 250°, and melts and decomposes at 262—264°, gives a blue coloration with ferric chloride in alcoholic solution, no coloration with bleaching powder, dissolves in cold concentrated sulphuric acid to a colourless solution which on warming becomes green to violet, reddens alcoholic litmus solution, and dissolves easily in aqueous sodium carbonate solution. Hæmatommin,  $C_{10}H_{16}O$  or  $C_{20}H_{32}O_2$ , forms a white, crystalline powder, melts at 143—144°, is sparingly soluble in ether, alcohol, or acetic acid, insoluble in aqueous potassium hydroxide or ammonia, and gives no colour reaction with ferric chloride or bleaching powder. Hæmatommidin crystallises in small, white needles, from hot alcohol in characteristic ball-like aggregates, melts at 194—196°, is easily soluble in ether, benzene, acetone, or hot glacial acetic acid, insoluble in aqueous potassium hydroxide or ammonia, gives no coloration with ferric chloride or bleaching powder, and dissolves in cold concentrated sulphuric acid to a yellow solution which becomes brown on warming.

*Ochrolechia pallescens* ( $\gamma$ ) *parella*, from Sandstein, near Trieste, and from Norway, contains ochrolechiasic acid, but no lecanoric acid (compare Schunck, *Annalen*, 1845, 54, 274).

Ochrolechiasic acid forms microscopic, white crystals, which lose 10 per cent. water of crystallisation at 120° and melt at 280°; it is much less soluble than parellic acid in hot alcohol, dissolves easily in hot glacial acetic acid, but is only sparingly soluble in ether. The alcoholic solu-

tion gives a purple coloration with ferric chloride; the solution in concentrated sulphuric acid becomes reddish-brown on warming. It is easily soluble in aqueous potassium hydroxide and is precipitated by addition of hydrochloric acid. On boiling with aqueous barium hydroxide, barium carbonate is precipitated and there remains in solution an amorphous substance which in alcoholic solution gives a purple coloration with ferric chloride.

G. Y.

2:4-Dinitrobenzaldehyde. II. By FRANZ SACHS and R. KEMPF (*Ber.*, 1902, 35, 2704—2717. Compare this vol., i, 376 and 377).—2:4-Dinitrobenzylidene-*o*-toluidine crystallises from amyl alcohol in long, lustrous, yellow needles and melts at 153.5° (corr.); 2:4-dinitrobenzylidenebenzidine crystallises from xylene in small, thin, striated plates of a reddish colour and melts at 186°, and the *bis*-2:4-dinitrobenzylidenebenzidine crystallises with 1 mol. of nitrobenzene in yellowish-red, silky needles or with 1 mol. of benzene in bright yellow, slender needles, losing the nitrobenzene or benzene of crystallisation at 120—130° and melting at 246°. The *semicarbazone* crystallises in long, slender needles and melts and decomposes at 265°.

Attempts to prepare the aldehyde or 2:4:6-trinitrobenzaldehyde by the electrolytic oxidation of the corresponding nitrotoluenes led only to the formation of the acids.

When reduced with ammonium sulphide, the aldehyde yields the compound  $C_7H_8ON_2$ , which crystallises in yellow laminae, melts at 152.5° (corr.), and probably has the constitution  $NH_2 \cdot C_6H_3 \begin{smallmatrix} < CH \cdot OH \\ NH \end{smallmatrix}$ ;

the *diacetyl* derivative crystallises in lustrous needles and melts at 235.5° (corr.), and, when treated with phenylhydrazine in glacial acetic acid solution, yields *diacetyldiaminobenzylidenephénylhydrazone*, which separates from nitrobenzene or acetic acid in yellow crystals melting and decomposing between 246° and 252° (corr.).

2:4-Nitroaminobenzaldehydesemicarbazone, obtained when the corresponding oxime (*loc. cit.*) is treated with semicarbazide, is a yellowish-red, crystalline powder which decomposes between 220° and 300° without melting; the *O,N*-*diacetyl* derivative of the oxime crystallises in almost colourless needles and melts at 174° (corr.).

When *o*-nitrobenzylideneaniline is exposed in benzene solution to a strong light for 8 days, a 44 per cent. yield of *o*-nitrosobenzoylanilide is obtained; 2:4-dinitrobenzylideneaniline similarly yields two undetermined compounds melting respectively at 289° (corr.) and 180.5° (corr.).

R. H. P.

Condensation of Nitromethane with Aromatic Aldehydes. By LOUIS BOUVEAULT and ANDRÉ WAHL (*Compt. rend.*, 1902, 135, 41—43).—Nitromethane readily condenses with aromatic aldehydes in presence of sodium methoxide and methyl alcohol, forming derivatives of the type  $OH \cdot CHR \cdot CH : NO \cdot ONa$ ; these dissolve without change in water but are decomposed by acids with liberation of the corresponding nitroalcohol, which, at the moment of its formation, is partially dehydrated, yielding compounds of the type  $CHR : CH \cdot NO_2$ . The dehydration is complete if the salts are boiled with zinc chloride dissolved in

glacial acetic acid. Anisaldehyde yields *p*-methoxy-*o*-nitrostyrene in yellow needles which melt at 80° and are reduced by zinc and acetic acid to *p*-methoxyphenylacetaldoxime, melting at 112°. Piperonylaldehyde yields *piperonylidene*nitromethane in yellow needles melting at 159°; when reduced, it yields the *oxime* of *homopiperonylaldehyde* melting at 120°. Furfuraldehyde yields *furfurylidene*nitromethane, which melts at 74° and boils at 135° under 20 mm. pressure; the *homofurfuraldoxime* which it yields on reduction forms long needles melting at 61–62° and boiling at 120–130° under 25 mm. pressure.

The sodium derivative of the nitroalcohol obtained in this way from *o*-nitrobenzaldehyde is not dehydrated by zinc chloride, but when distilled in a vacuum it yields *o*-*o*-dinitrostyrene, melting at 106–107° and boiling at about 200° under 20 mm. pressure. C. H. B.

**Constitution of Auramine and the Salts of Phenyliminobenzophenone.** By CARL GRAEBE (*Ber.*, 1902, 35, 2615–2621. Compare *Abstr.*, 1899, i, 702).—The close resemblance existing between the salts of auramine and phenyliminobenzophenone renders the quinonoid constitution of the former very doubtful, since it is not possible to formulate the latter on this type. The production of a very stable hydrated hydrochloride of phenyliminobenzophenone is not decisive evidence in favour of the quinonoid view (compare Dimroth and Zoeppritz, this vol., i, 292), since anhydrous salts of this imine may be readily obtained. The anhydrous *hydrochloride*,  $\text{CPh}_2\text{:NPh}\cdot\text{HCl}$ , prepared by leading hydrogen chloride into a benzene solution of the imine, is a pale yellow precipitate melting at 190°; it dissolves in chloroform to an intensely yellow solution. The *hydriodide*,  $\text{CPh}_2\text{:NPh}\cdot\text{HI}$ , produced by shaking the benzene solution of the imine with dilute hydriodic acid, melts and decomposes at 185°. The *methiodide*, formed by heating its generators on the water-bath, separates in deep yellow crystals melting at 202°; when heated with alkali hydroxides or carbonates, it is hydrolysed into benzophenone and methylaniline. *Auramine methiodide*,  $(\text{NMe}_2\cdot\text{C}_6\text{H}_4)_2\text{C:NH}\cdot\text{MeI}$ , obtained either by mixing its generators at the ordinary temperature or by heating them in benzene solution at 100°, separates in deep yellow crystals and melts at 235–240°; it dissolves in hot water or in hydrochloric acid, but is insoluble in benzene. A trimethiodide, produced by the action of excess of methyl iodide, separates in yellow crystals and melts at 165°.

The monomethiodide must be regarded as the hydriodide of methylauramine, for it yields this substance on treatment with dilute sodium hydroxide solution; the new base closely resembles auramine and melts at 130°. Phenylauramine may be readily prepared by heating tetramethyldiaminobenzophenone with aniline at the boiling point of the latter; its *hydriodide*, produced by double decomposition from potassium iodide and the chloride, separates in anhydrous, yellow crystals melting at 242°; the *methiodide*,  $(\text{NMe}_2\cdot\text{C}_6\text{H}_4)_2\text{C:NPh}\cdot\text{MeI}$ , obtained by heating an equivalent proportion of its generators in benzene solution at 100°, separates in red crystals melting at 214°; on hydrolysis, it yields tetramethyldiaminobenzophenone and methyl aniline, this result indicating that in the methiodide the

methyl iodide is attached to the iminic nitrogen. When phenylauramine is warmed with excess of methyl iodide at  $100^\circ$ , a *trimethiodide*,  $(\text{NMe}_3\text{I}\cdot\text{C}_6\text{H}_4)_2\text{C}\cdot\text{NPh}\cdot\text{MeI}$ , is produced which separates in ruby-red crystals; this salt, when dried at  $100^\circ$ , loses rather more than one mol. of methyl iodide, at  $120^\circ$  a second mol. is removed, and the composition of the product approximately corresponds with that of the monomethiodide.

G. T. M.

**Derivatives of Desylamine and of Phenanthraquinone.** By ROBERT PSCHORR and FRITZ BRÜGGEMANN (*Ber.*, 1902, 35, 2740—2744. Compare Gabriel and Neumann, *Abstr.*, 1890, 890).—Desylamine,  $\text{COPh}\cdot\text{CHPh}\cdot\text{NH}_2$ , may be obtained by the reduction of an alcoholic solution of benzilmonoxime with stannous chloride and concentrated hydrochloric acid. The hydrochloride crystallises in needles on the addition of ether to its alcoholic solution and melts at  $243^\circ$  (corr.), not at  $209^\circ$ . Its solubility in hot alcohol is 1 : 7, in cold alcohol 1 : 12, and in cold water 1 : 20. The free base melts at  $109^\circ$  (corr.) and crystallises from ether in needles. It combines with phenylcarbimide, yielding *desylphenylcarbamide* melting at  $174$ — $175^\circ$  (corr.). *Desylaminephenylhydrazone* crystallises from acetic acid in small, yellow needles melting at  $226$ — $227^\circ$  (corr.).

The *benzoyl* ester of phenanthraquinoneoxime crystallises in needles melting at  $174$ — $175^\circ$  (corr.), and when reduced yields 9 : 10-amino-phenanthrol. The additive *compound* of phenanthraquinoneoxime and phenylcarbimide crystallises from benzene in needles melting at  $127$ — $128^\circ$ , and on reduction yields aminophenanthrol.

When methylated, the oxime yields the *anhydride* of phenanthraquinoneoxime methyl ether,  $\text{C}_{14}\text{H}_8\langle\text{N}\rangle\text{CH}$ , melting at  $145$ — $146^\circ$  (compare Moldauer, *Abstr.*, 1897, i, 42).

J. J. S.

**Crystallography of the Borneols and of their Esters and of Chloral and Bromal Bornylate.** By JULES MINGUIN (*Bull. Soc. Chim.*, 1902, [iii], 27, 683—689).—In preparing artificial *d*-borneol from the mixture of this with *l*-isoborneol which is obtained by the hydrogenisation of camphor, the author makes use of the fact that the *isoborneol* is much more rapidly oxidised by chromic acid than is *d*-borneol.

The succinate of artificial *d*-borneol crystallised from light petroleum forms hexagonal plates modified by rhombohedral faces; crystallised from methyl alcohol, it forms rhombic prisms [ $a:b:c = 0.91633:1:0.77067$ ]. *l*-Bornyl succinate is perfectly similar to the *d*-compound. The succinates of the *isoborneols* form hexagonal plates isomorphous with those of the borneols, but no rhombic prisms have been obtained in the case of the *isoborneols*. The crystals of *r*-bornyl succinate differ from those given above, but the angles could not be measured on account of the opacity of the crystals. *d*-Bornyl phthalate crystallises in the rhombic system [ $a:b:c = 0.85605:1:2.3407$ ]. *l*-Bornyl phthalate has the same crystalline form, but the author believes that plagiohemihedry is also present.

The campholates of chloral are not isomorphous with those of

bromal, although the campholates and *isocampholates* are in each case isomorphous. Bromal campholate and *isocampholate* crystallise in monoclinic prisms [ $a:b:c = 1.1697:1:1.0600$ ;  $\beta = 96^\circ 15'$ ]. A. F.

**Crystallography of the Brominated Derivatives of Benzylidenecamphor and of Benzylcamphor.** By JULES MINGUIN (*Bull. Soc. Chim.*, 1902, [iii], 27, 679—681).—Bromobenzilidenecamphor crystallises in rhombic prisms [ $a:b:c = 0.59494:1:0.3994$ ]. Bromobenzylcamphor crystallises in rhombic prisms [ $a:b:c = 0.9462:1:0.8846$ ]; *o*-bromobenzylidenecamphor crystallises in monoclinic prisms [ $a:b:c = 0.97679:1:0.5585$ ;  $\beta = 107^\circ 28'$ ]. *p*-Bromobenzylidenecamphor forms rhombic prisms [ $a:b:c = 0.8068:1:1.455$ ]. No hemihedral faces have been observed in the case of the above compounds, but, nevertheless, their internal structure is asymmetric. A. F.

**Fenchene.** By OTTO WALLACH (*J. pr. Chem.*, 1902, [ii], 65, 586—596).—Polemical. A reply to Kondakoff (this vol., i, 478).

G. Y.

**Cinnamon Oil from Ceylon.** By HEINRICH WALBAUM and O. HÜTHIG (*J. pr. Chem.*, 1902, [ii], 66, 47—58).—In addition to cinnamaldehyde, the authors have obtained the following from cinnamon oil from Ceylon:—Methyl amyl ketone, pinene, phellandrene, cymene, benzaldehyde, linalool, caryophyllene, cuminaldehyde, and eugenol. They also found indications of the presence of a higher fatty aldehyde (probably nonylaldehyde), furfuraldehyde, phenylpropaldehyde, and isobutyric acid (as an ester). R. H. P.

**Sugars from Crocin and Picrocrocin.** By JAROSLAV KASTNER (*Zeit. Zuckerind. Böhm.*, 1902, 26, 538—541).—A careful examination of the sugar produced by the hydrolysis of crocin and picrocrocin has shown that in each case it consists of dextrose only. E. G.

**Constitution of Aloins: Comparison with that of Glucosides.** By EUGÈNE LÉGER (*Compt. rend.*, 1902, 134, 1584—1586. Compare this vol., i, 549).—Besides isohydroxymethylchrysin (trihydroxymethylantraquinone), there is formed in the action of sodium peroxide on barbaloin and its isomerides, formic acid and a laevorotatory substance having the composition of an aldopentose.

The author suggests that barbaloin is represented by the expression

$$\text{CH}:\text{CH}:\text{C}:\text{CO}:\text{C}:\text{C}(\text{OH}):\text{CH}:\text{CMe}$$

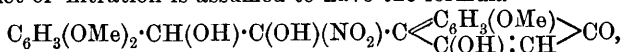
$$\text{OH}:\text{C}=\text{CH}:\text{C}:\text{CO}:\text{C} \begin{array}{c} \text{||} \\ \text{C} \end{array} \text{O}:\text{CHMe}(\text{CH}:\text{OH})_3:\text{CHO} ;$$
 the empirical formula should then be  $\text{C}_{21}\text{H}_{20}\text{O}_9$ , and not  $\text{C}_{16}\text{H}_{16}\text{O}_7$  which has been previously used. Further, chlorobarbaloin has the formula  $\text{C}_{21}\text{H}_{16}\text{O}_9\text{Cl}_4$ , and its acetyl derivative  $\text{C}_{21}\text{H}_{11}\text{O}_9\text{Cl}_4\text{Ac}_5$ ; the mol. weight of the last-mentioned substance (in benzene) is in agreement with this formula. Attention is drawn to the fact that these aloins resemble glucosides in constitution, but, unlike them, are not hydrolysable by dilute acids.

In ethyl acetate, barbaloin has  $[\alpha]_D - 10.4^\circ$ , in water  $+ 21.4^\circ$ ; *iso*-barbaloin has  $[\alpha]_D - 19.4^\circ$  in ethyl acetate, but is inactive in aqueous solution. It is suggested that *isobarbaloin* differs from barbaloin in

the position of attachment of the sugar group to the anthraquinone nucleus; in the former, the point of attachment is probably at position 6.

Both nataloin and homonataloin are optically active; in ethyl acetate, nataloin has  $[\alpha]_D -107.7^\circ$ , and homonataloin  $[\alpha]_D 112.6^\circ$ ; it seems most probable that these substances are respectively represented by the formulæ  $C_{23}H_{26}O_{10}$  and  $C_{22}H_{24}O_{10}$ . K. J. P. O.

**The Degradation of Brazilin.** By STANISLAUS VON KOSTANECKI and LUDWIG PAUL (*Ber.*, 1902, **35**, 2608—2611. Compare this vol., i, 482, and Gilbody and Perkin, *Trans.*, 1902, **31**, 1049).—The oxidation product,  $C_{19}H_{18}O_6$ , of trimethylbrazilin, when treated with cold nitric acid yields the nitrogenous substance  $C_{19}H_{19}O_6N$ , which, on warming with solutions of the alkali hydroxides, becomes decomposed into *p*-methoxysalicylic acid and two neutral nitro-compounds. These substances, 6-nitrohomoveratrol and *tetramethoxydinitrodibenzyl*, are separated by treatment with alcohol in which solvent the latter is insoluble. The dinitro-compound crystallises from glacial acetic acid or benzene and alcohol in white needles and melts at  $206^\circ$ . The initial product of nitration is assumed to have the formula



and results from the fission of the indanediole nucleus of the compound  $C_{19}H_{18}O_6$ , the reaction being accompanied by the addition of a mol. of nitric acid; this nitro-compound should on hydrolysis give rise to *p*-methoxysalicylic and glycollic acids together with 6-nitrohomoveratrol; its precise relationship to the dibenzyl derivative has not yet been definitely determined. G. T. M.

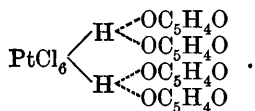
**Oxonium Theory.** By ALFRED COEHN (*Ber.*, 1902, **35**, 2673—2677).—The electrolysis of a solution of dimethylpyrone hydrochloride seems to decide whether this substance is a molecular compound or a true salt, since in the latter case the dimethylpyrone will migrate along with the hydrogen as a complex positive ion to the cathode. This actually occurs when a solution of 60 grams of dimethylpyrone hydrochloride in 250 grams of 20 per cent. hydrochloric acid is electrolysed, and the accumulation of dimethylpyrone at the cathode takes place both when the cathode is separated from the solution by a membrane and when no membrane is present. In the experiments, the effect of diffusion was allowed for, and the disappearance of dimethylpyrone from the neighbourhood of the anode was also observed. A. H.

**Constitution of Oxonium Salts.** By ALFRED WERNER (*Annalen*, 1902, **322**, 296—351. Compare this vol., ii, 50).—The hypothesis of supplementary valency is employed in explaining the production of the oxonium compounds.

Pyrone, when treated with platinic chloride in concentrated aqueous solution, gives rise to the crystalline *platinichloride*,  $C_{20}H_{14}O_8 \cdot H_2PtCl_6$ , which separates in flesh-coloured leaflets. The formation of this compound, which contains four mols. of pyrone, is not readily explic-



able on the assumption that it contains quadrivalent oxygen. According to the author's theory, the combination occurs through the agency of the supplementary valencies of the pyrone oxygen and the hydrogen of the chloroplatinic acid, the substance produced having the coordination formula :



*Dimethylpyrone cupric chloride*,  $\text{C}_7\text{H}_8\text{O}_2\text{CuCl}_2$ , separates in brownish-yellow needles on adding dimethylpyrone to a saturated cupric chloride solution, and similar compounds are obtained with other metallic chlorides. Their formation is assumed to be due to the supplementary valency of the metallic radicle and the pyrone oxygen, the copper compound having the formula  $\text{O}\cdot\text{C}_7\text{H}_8\text{O}\cdots\text{CuCl}_2$ .

[With KALKMANN.]—The hexacarbaminochromic salts first discovered by Sell have been re-examined from the author's standpoint and the following derivatives are described.

The *bromide*,  $[\text{Cr}(\text{CON}_2\text{H}_4)_6]\text{Br}_3\cdot 3\text{H}_2\text{O}$ , prepared by treating the corresponding chloride with potassium bromide in aqueous solution, crystallises in pale green, soluble needles; the electrical conductivity at  $25^\circ$  is  $\mu_{125} = 290\cdot 18$  and  $\mu_{1000} = 335\cdot 0$ .

The *iodide*,  $[\text{Cr}(\text{CON}_2\text{H}_4)_6]\text{I}_3$ , also obtained from the chloride, crystallises in lustrous, bluish-green needles; it is more stable than the other halogen salts, and may be heated at the temperature of the water-bath without undergoing decomposition; its electrical conductivity at  $25^\circ$  is  $\mu_{125} = 287\cdot 2$  and  $\mu_{1000} = 338\cdot 7$ .

The *thiocyanate*,  $[\text{Cr}(\text{CON}_2\text{H}_4)_6](\text{SCN})_3$ , formed by double decomposition from the chloride and potassium thiocyanate, crystallises from water in green needles; the electrical conductivity at  $25^\circ$  is  $\mu_{125} = 269\cdot 61$  and  $\mu_{1000} = 325\cdot 55$ .

The double salt (*hexacarbaminochromic chromihexathiocyanate*),  $[\text{Cr}(\text{CON}_2\text{H}_4)_6][\text{Cr}(\text{SCN})_6]$ , is produced by allowing a solution of the preceding salt to remain for four weeks, or more rapidly by heating the salt either alone or in solution, the decomposition of the dry compound at  $90^\circ$  being completed in four minutes; it is also obtained by mixing solutions of the preceding compound and chromic thiocyanate. The product is an amorphous, pale red powder insoluble in water and the other ordinary solvents.

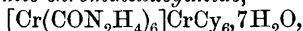
The hexacarbaminochromic chloride,  $[\text{Cr}(\text{CON}_2\text{H}_4)_6]\text{Cl}_3\cdot 3\text{H}_2\text{O}$ , from which the preceding salts are prepared, is produced by treating the product,  $\text{Cr}(\text{CON}_2\text{H}_4)_6(\text{Cr}_2\text{O}_7)\text{Cl}\cdot 6\text{H}_2\text{O}$ , of the action of chromyl chloride on carbamide with moist lead chloride; it crystallises in pale green needles belonging to the monoclinic system and decomposes at  $155^\circ$ ; its electrical conductivity at  $25^\circ$  is  $\mu_{125} = 296\cdot 52$  and  $\mu_{1000} = 340\cdot 47$ .

The *nitrite*,  $[\text{Cr}(\text{CON}_2\text{H}_4)_6](\text{NO}_2)_3$ , is produced by mixing solutions of the chloride with sodium nitrite or the fumes evolved from arsenious oxide and nitric acid; it closely resembles the chloride; its electrical conductivity at  $25^\circ$  is  $\mu_{125} = 269\cdot 7$  and  $\mu_{1000} = 324\cdot 2$ .

The *cyanide*,  $[\text{Cr}(\text{CON}_2\text{H}_4)_6](\text{CN})_3\cdot 5\frac{1}{2}\text{H}_2\text{O}$ , also produced by double

decomposition, crystallises in dark-green needles; it is very unstable, melts at 75°, and has an odour of hydrogen cyanide.

*Hexacarbaminochromic chromihexacyanide*,



slowly separates from a solution of the preceding cyanide in the form of small, greenish-yellow, sphenoid crystals; it still contains the carbaminochromium complex, yielding the characteristic nitrate and chloride on treatment with nitric and hydrochloric acids respectively.

The *hexahydrated salt*,  $[\text{Cr}(\text{CON}_2\text{H}_4)_6]\text{CrCy}_6, 6\text{H}_2\text{O}$ , obtained by adding potassium chromicyanide to a solution of hexacarbaminochromic chloride, is a pale green powder insoluble in cold water and dissolving only slowly in the warm solvent.

The *permanganate*,  $[\text{Cr}(\text{CON}_2\text{H}_4)_6](\text{MnO}_4)_3$ , produced from the chloride by the interaction of potassium permanganate, is a dark violet, lustrous precipitate readily decomposed on warming.

The *chloride-sulphate*,  $[\text{Cr}(\text{CON}_2\text{H}_4)_6]\text{Cl}_2\text{SO}_4, 2\text{H}_2\text{O}$ , prepared by mixing solutions of the chloride and a soluble sulphate, crystallises from hot water in lustrous, greenish-blue needles rapidly decomposing on exposure.

The *hydrogen sulphate*,  $[\text{Cr}(\text{CON}_2\text{H}_4)_6]\text{H}(\text{SO}_4)_2, 3\text{H}_2\text{O}$ , obtained by adding excess of sulphuric acid to a solution of the preceding salt, crystallises from water acidified with this acid in pale green, prismatic needles.

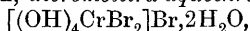
The *double salt*,  $[\text{Cr}(\text{CON}_2\text{H}_4)_6][\text{CO}(\text{NO}_2)_4(\text{NH}_3)_2]_3, 3\text{H}_2\text{O}$ , prepared by adding hexacarbaminochromic chloride to a concentrated solution of diammoniocobaltic tetranitrite, separates as a yellowish-brown precipitate which, when crystallised from water in small portions, forms dark yellow needles with a golden lustre decomposing at 100°.

The *double salt*,  $[\text{Cr}(\text{CON}_2\text{H}_4)_6][\text{CO}(\text{NO}_2)_4(\text{NH}_3)_2]\text{Cl}_3, 3\text{H}_2\text{O}$ , produced by reversing the order of mixing employed in the preceding preparation, is a more soluble compound crystallising in slender, pale yellow needles.

The *polysulphide*,  $\text{C}_6\text{O}_6\text{N}_{12}\text{H}_{24}\text{CrS}_6$ , is an amorphous, dark green precipitate, obtained by treating the chloride with yellow ammonium sulphide.

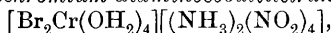
[With A. GUBSER.]—The two isomeric hydrated chromium bromides,  $\text{CrBr}_3, 6\text{H}_2\text{O}$ , described by Recoura (Abstr., 1890, 1063) were shown by determinations of the electrical conductivity to be structurally dissimilar.

The green modification, *dibromotetra-aquochromium bromide*,



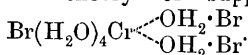
behaves as a salt containing two ions; the values of  $\mu_{125}$  vary from 70.7 to 79.5. This compound, however, undergoes hydrolytic dissociation much more rapidly than the corresponding green chloride, and hence the amount of bromine precipitable by silver nitrate is greater than that demanded by the formula.

The blue modification, *hexa-aquochromium bromide*,  $[\text{Cr}(\text{OH}_2)_6]\text{Br}_3$ , is extremely hygroscopic, and, contrary to Recoura's description, is readily soluble in alcohol; it behaves as a salt containing 4 ions,  $\mu_{125}$  being 173. The whole of its halogen is precipitable by silver nitrate even in cold solutions.

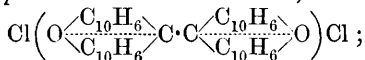
*Dibromotetra-aquochromium diaminocobaltitetranitrite,*

produced by mixing together warm solutions of diaminocobaltic tetranitrite and the green chromium bromide, is precipitated in dark green crystals readily soluble in water, alcohol, or acetone.

The *double salt*,  $[\text{OH}_2 \cdot \text{CrBr}_5]\text{Rb}_2$ , prepared by evaporating down in a current of hydrogen bromide a solution of rubidium bromide,  $\text{RbBr}$ , and the green chromium bromide, is a brownish-violet, crystalline compound, dissolving in water to a red solution, the colour of which rapidly changes to green. A green double salt has also been obtained, but its composition is not yet ascertained. The transformation of the green hydrate into its blue isomeride is thus indicated according to the theory of supplementary valency,  $\text{Br}(\text{H}_2\text{O})_4\text{CrBr}_2 + 20\text{H}_2 =$

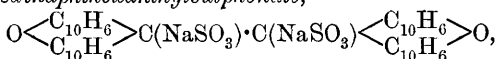


*Chloral-β-dinaphthyleneoxide*, when oxidised with manganese dioxide and hydrochloric acid in hot glacial acetic acid solution, yields a reddish-brown salt, *bisdinaphthoxanthoxonium chloride*,



this substance is soluble in hot concentrated hydrochloric acid and separates in small, red crystals with a green reflex; in this form, it has the composition  $\text{C}_{42}\text{H}_{24}\text{O}_2\text{Cl}_2 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$ . The *methyl ether*,  $\text{C}_{44}\text{H}_{30}\text{O}_4$ , is readily produced by boiling the salt with methyl alcohol; the *ethyl ether*,  $\text{C}_{46}\text{H}_{34}\text{O}_4$ , is prepared in a similar manner; these substances melt respectively at  $158^\circ$  and  $147^\circ$ , and are reconverted into yellow oxonium salts by the action of mineral acids.

*Bisdinaphthoxanthylene*,  $\text{O} \begin{array}{c} \diagup \text{C}_{10}\text{H}_6 \\ \diagdown \text{C}_{10}\text{H}_6 \end{array} \text{C} : \text{C} \begin{array}{c} \diagup \text{C}_{10}\text{H}_6 \\ \diagdown \text{C}_{10}\text{H}_6 \end{array} \text{O}$ , prepared by reducing the preceding ethers with zinc dust and glacial acetic acid, crystallises in white needles which commence to decompose at  $270^\circ$  but do not melt below  $300^\circ$ ; halogens or nitrous fumes reconvert it into oxonium salts.

*Sodium bisdinaphthoxanthylsulphonate,*

produced by triturating the oxonium chloride with a concentrated solution of sodium hydrogen sulphite, crystallises from hot water either in long, white needles or thin, monoclinic plates; it decomposes at  $100^\circ$ , changing into a red substance which is probably an oxonium sulphite.

The *potassium salt*,  $\text{C}_{42}\text{H}_{24}\text{O}_6\text{S}_2\text{K}_2 \cdot 10\text{H}_2\text{O}$ , crystallises from water in small, nacreous leaflets which become coppery-red at  $100^\circ$ , the coloured product, however, when crystallised from hot water, again regenerates the colourless salt.

Mineral acids convert these sulphonates into the reddish-yellow oxonium salts.

G. T. M.

**Oxidising Properties of a Pyranol.** By ROBERT FOSSE (*Compt. rend.*, 1902, 135, 39–41).—The action of hydriodic acid on dinaphthapyranol does not yield dinaphthapyranoxonium, but the oxonium

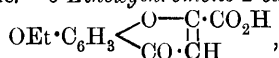
tri-iodide (1 mol.) and dinaphthapyran (2 mols.). When dinaphthapyranol is boiled with diphenopyranol in presence of acetic acid, the former is reduced to dinaphthapyran, whilst the latter is oxidised to diphenopyrone. C. H. B.

**A Tetrahydroxyflavone Dye.** By STANISLAUS VON KOSTANECKI and E. PLATTNER (*Ber.*, 1902, 35, 2544—2546).—2 : 4-Diethoxy-3' : 4' : 5'-trimethoxybenzoylacetophenone,  $\text{C}_6\text{H}_3(\text{OEt})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_2(\text{OMe})_3$ , prepared by the action of sodium on a mixture of resacetophenone diethyl ether, and ethyl trimethylgallate, crystallises from a mixture of acetic acid and alcohol in long, pale yellowish needles, which melt at  $132.5^\circ$  and give a dirty red colour with alcoholic ferric chloride.

3 : 3' : 4' : 5'-Tetrahydroxyflavone, 
$$\begin{array}{c} \text{OH} \cdot \text{CH} : \text{CH} : \text{CO} - \text{C} \cdot \text{C}_6\text{H}_2(\text{OH})_3 \\ | \quad | \quad | \\ \text{CH} : \text{CH} : \text{C} \cdot \text{CO} \cdot \text{CH} \end{array}$$
, pre-

pared by the action of hydriodic acid on the preceding compound and purified by conversion into the methyl ether, crystallises from hot dilute alcohol in white needles, with  $1\text{H}_2\text{O}$ , and melts and decomposes at  $340^\circ$ . The tetramethyl ether,  $\text{C}_{19}\text{H}_{18}\text{O}_6$ , crystallises in needles and melts at  $191$ — $192^\circ$ . The tetra-acetyl compound,  $\text{C}_{23}\text{H}_{18}\text{O}_{10}$ , crystallises from alcohol in snow-white flakes and melts at  $215^\circ$ . T. M. L.

**2-Hydroxychromone.** By E. DAVID and STANISLAUS VON KOSTANECKI (*Ber.*, 1902, 35, 2547—2549).—Ethyl 2-hydroxy-5-ethoxybenzoylpyruvate,  $\text{OEt} \cdot \text{C}_6\text{H}_4(\text{OEt}) \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CO}_2\text{Et}$ , prepared from quinacetophenone monoethyl ether and ethyl oxalate, crystallises from dilute alcohol in needles, melts at  $92^\circ$ , and gives a dirty red colour with alcoholic ferric chloride. 6-Ethoxychromone-2-carboxylic acid,



prepared by the action of hydrochloric acid on an alcoholic solution of the preceding compound, crystallises from alcohol in needles, with  $1\text{H}_2\text{O}$ , and melts at  $235^\circ$  with liberation of carbon dioxide. 6-Ethoxy-

chromone,  $\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{array}{l} \text{O} - \text{CH} \\ \diagup \quad | \\ \text{CO} \cdot \text{CH} \end{array}$ , crystallises from alcohol in glistening,

thin tablets, which gradually become dull and crumble and melt at

$89$ — $90^\circ$ . 6-Hydroxychromone,  $\text{OH} \cdot \text{C}_6\text{H}_3 \begin{array}{l} \text{O} - \text{CH} \\ \diagup \quad | \\ \text{CO} \cdot \text{CH} \end{array}$ , crystallises from

dilute alcohol in white needles, melts at  $243$ — $244^\circ$ , and dissolves in dilute sodium hydroxide to a pale yellow solution. The acetyl derivative,  $\text{C}_{11}\text{H}_8\text{O}_4$ , crystallises from dilute alcohol in white needles and melts at  $126$ — $127^\circ$ . T. M. L.

**Acyl Derivatives of isoPyromucic Acid:** isoPyromucyl Acetate, Benzoate, and Pyromucate. By G. CHAVANNE (*Compt. rend.*, 1902, 134, 1511—1512).—isoPyromucyl acetate,  $\text{COMe} \cdot \text{O} \cdot \text{C}_6\text{H}_3\text{O}_2$ , obtained by heating isopyromucic acid with acetyl chloride or acetic anhydride, boils at  $152^\circ$  under 20 mm. pressure, melts at  $28^\circ$ , is easily soluble in the common organic solvents and very readily so in water, is neutral, and gives no coloration with ferric chloride. It can be easily saponified; with alcohol, in presence of hydrochloric acid, it gives

ethyl acetate and *isopyromucic acid*; with phenylhydrazine, it gives acetylphenylhydrazine, and with aniline, acetanilide. It resembles phenyl acetate rather than the alcoholic acetates (esters).

*isoPyromucyl benzoate*,  $\text{COPh}\cdot\text{O}\cdot\text{C}_5\text{H}_3\text{O}_2$ , obtained by heating *isopyromucic acid* with benzoyl chloride, crystallises from alcohol in prisms which melt at  $85^\circ$ , cannot be distilled, and is soluble in organic solvents but almost insoluble in water. It can be easily saponified and reacts with alcohol or phenylhydrazine just as the acetate does.

*isoPyromucyl pyromucate*,  $\text{C}_4\text{H}_3\text{O}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_5\text{H}_3\text{O}_2$ , produced by heating *isopyromucic acid* with pyromucyl chloride at  $150^\circ$  for three hours, is soluble in alcohol, and can be precipitated by water. It melts at  $99^\circ$  and behaves towards reagents just as the acetate does.

These observations confirm the conclusion already arrived at that *isopyromucic acid* has a phenolic (enolic) character. J. McC.

**Ammonium Compounds. VIII. History of Hydroxydihydro-bases.** By HERMAN DECKER (*Ber.*, 1902, 35, 2588—2589).—A summary of the author's views on the action of alkalis on the methiodides of *cycloamine* bases (compare Abstr., 1893, i, 115).

T. M. L.

**Ammonium Compounds. IX. Theory of Hydroxydihydro-bases.** By HERMAN DECKER (*Ber.*, 1902, 35, 2589—2593).—The assumption made by Roser (Abstr., 1893, i, 177) that the hydroxydihydro-bases of the pyridine and quinoline series are aldehyde bases,  $\text{R}(\text{NHMe})\cdot\text{C}:\text{C}:\text{CHO}$ , produced by ring-fission is unnecessary, because similar derivatives of the acridine group are known, and in this case the opening of the heterocyclic ring is not possible. These carbinol bases of the dihydroacridine series, however, behave in all respects precisely like the supposed aldehyde bases, and under the influence of alkalis undergo the characteristic transformation into methylidihydro-acridine and methylacridone (Pictet and Patry, this vol., i, 644). The parallelism between the hydroxydihydro-bases of the pyridine and quinoline group on the one hand and hydrastinine and cotarnine on the other is maintained providing that the bases of both series are assumed to have the closed chain formula, with the reservation that in certain reactions they undergo an intermediate ring-fission. In accordance with this hypothesis, hydrastinine should have the carbinol constitution  $\text{CH}_2\begin{matrix} \text{O}\cdot\text{C}\cdot\text{CH}:\text{C}\cdot\text{CH}_2 \\ \text{O}\cdot\text{C}\cdot\text{CH}:\text{C}\cdot\text{CH}(\text{OH})\cdot\text{NMe} \end{matrix}$  whilst the papaveriniumalkylhydroxides of Goldschmidt and Strausky should have formulæ corresponding with  $\text{CH}\begin{matrix} \text{O}\cdot\text{C}\cdot\text{CH}:\text{C}\cdot\text{CH}_2 \\ \text{O}\cdot\text{C}\cdot\text{CH}:\text{C}\cdot\text{CH}(\text{OH})\cdot\text{NMe} \end{matrix}$  (Abstr., 1888, 1116; 1889, 166; 1890, 179). Roser supposes that the isomeric change of ammonium base to carbinol derivative is due to the successive elimination and addition of water. This theory does not, however, account for the formation of carbinol ethers from the methiodides dissolved in absolute alcohol. The author is inclined to accept Hantzsch's ionisation theory, providing that it can be shown that the ionised part of the ammonium base undergoes only very slight isomerisa-

tion. The experimental evidence shows that the pyridinium and quinolinium hydroxides are comparatively stable in dilute aqueous solutions, and undergo isomeric change when these solutions are concentrated or when non-electrolytes are added. The alkali hydroxides produce a similar result, and these substances also tend to diminish the ionisation of the ammonium base.

G. T. M.

**Cinnamylquinine Hydrochloride.** KALLE & Co. (D.R.-P. 131595).—*Cinnamylquinine hydrochloride*,  $C_{29}H_{30}O_5N_2 \cdot HCl$ , produced by adding cinnamyl chloride to quinine suspended in benzene, crystallises from hot water in white needles and melts at  $235-236^\circ$ .

Cinnamylquinine is set free by the action of sodium carbonate solution on the hydrochloride.

G. T. M.

**Action of Alcoholic Hydrogen Chloride on the Cerite Oxides.** By RICHARD JOS. MEYER and M. KOSS (*Ber.*, 1902, 35, 2622—2626).—The very soluble chlorides of the cerite metals are readily obtained in a crystallised form by the use of alcoholic hydrogen chloride, and, moreover, the employment of this reagent permits of the isolation of double compounds of these chlorides with the organic amines. The pyridine derivatives are particularly characteristic, and their stability varies directly as the basic nature of the metallic radicle, the lanthanum double salt being most stable.

Strongly ignited didymium oxide dissolves in warm absolute alcohol saturated with hydrogen chloride, and the solution on cooling deposits the *alcoholate*,  $DiCl_3 \cdot 3EtOH$ ; this salt dissolves in alcoholic hydrogen chloride to a green solution, which, on treatment with pyridine, yields colourless needles of the pyridine double salt.

Black praseodymium peroxide dissolves only slowly in the solvent, the action being accompanied by reduction and the liberation of chlorine; the addition of pyridine to the solution leads to the formation of a double salt,  $PrCl_3 \cdot 3(C_5H_5N \cdot HCl)$ , crystallising with an indeterminate amount of alcohol.

Neodymium oxide readily dissolves to a clear blue solution, and the *pyridine salt*,  $NdCl_3 \cdot 3(C_5H_5N \cdot HCl)$ , separating in blue needles, is more stable than the praseodymium derivative.

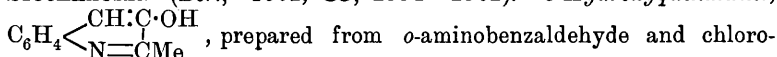
Alcoholic hydrogen chloride scarcely attacks cerium dioxide, but dissolves cerous carbonate, yielding a solution from which a sparingly soluble alcoholate separates; this compound rapidly loses alcohol on treatment with water, giving rise to the hydrated chloride  $2CeCl_3 \cdot 15H_2O$ ; the *pyridine double salt*,  $CeCl_3 \cdot C_5H_5N \cdot HCl \cdot 2EtOH$ , separates in white, hygroscopic needles.

Lanthanum chloride, whether as hydrate or alcoholate, is very soluble in alcoholic hydrogen chloride, and consequently only concentrated solutions of the oxide yield the *chloride*  $LaCl_3 \cdot 2EtOH$ ; the *hydrated salt*,  $2LaCl_3 \cdot 15H_2O$ , corresponds with the analogous cerous compound. The *pyridine double salt*,  $2LaCl_3 \cdot 3(C_5H_5N \cdot HCl) \cdot 2EtOH$  closely resembles the cerium derivative in outward appearance.

The *hydrated chlorides* of didymium and neodymium each contain  $6H_2O$ ; the corresponding praseodymium salt crystallises with  $7H_2O$ .

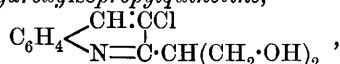
G. T. M.

**$\beta$ -Hydroxyquinaldine.** Condensation of  $\beta$ -Chloroquinaldine with Formaldehyde. By WILHELM KOENIGS and FERDINAND STOCKHAUSEN (*Ber.*, 1902, 35, 2554—2562).—3-Hydroxyquinaldine,



acetone, crystallises from hot dilute alcohol in glistening, pale yellow, odourless needles, becomes yellow at  $240^\circ$ , sinters and darkens at  $250^\circ$ , melts at  $260^\circ$  to a black liquid, and can be sublimed in small quantities in snow-white needles. The *platinichloride*,  $(\text{C}_{10}\text{H}_9\text{ON})_2, \text{H}_2\text{PtCl}_6, 2\text{H}_2\text{O}$ , forms glistening, orange-coloured needles or flakes, becomes dark, and melts with frothing at about  $210^\circ$ . The *hydrochloride* forms white, glistening, felted needles, begins to darken at  $200^\circ$ , sinters, becomes bluish-black, and finally melts to a black liquid at  $265^\circ$ . The *sulphate* crystallises from hot dilute sulphuric acid in beautiful, small needles containing water of crystallisation which is driven off at  $140\text{--}145^\circ$ , and melts at  $192\text{--}193^\circ$ . The *picrate* crystallises from alcohol in small, yellow, glistening needles, which darken, and then melt at  $245\text{--}246^\circ$  with vigorous frothing. The *ethyl ether* forms glistening, white, thin needles, which effloresce in air and sinter and melt at  $69\text{--}70^\circ$ .

3-Chloro-2- $\alpha$ -dihydroxyisopropylquinoline,



prepared from 3-chloroquinaldine and formaldehyde, crystallises from hot water in long, white needles with a slightly yellow tint, which sinter and then melt at  $122\text{--}123^\circ$ ; it melts under water to a yellowish oil, and yields formaldehyde when heated in a test-tube. The *platini-chloride*,  $(\text{C}_{12}\text{H}_{12}\text{O}_2\text{NCl})_2, \text{H}_2\text{PtCl}_6, 2\text{H}_2\text{O}$ , forms small, red needles, sinters, blackens, and melts with frothing at  $173^\circ$ . The *aurichloride* forms golden-yellow, glistening, flat needles, sinters, and melts to a yellow liquid at  $156^\circ$ . The *picrate* forms beautiful, yellow needles, and sinters and melts at  $147^\circ$ .

T. M. L.

**Action of Alkyl Iodides on Tetrahydroquinolinecarboxylic Acids.** By OTTO FISCHER and RUDOLPH ENDRES (*Ber.*, 1902, 35, 2611—2614. Compare Fischer, *Abstr.*, 1899, i, 641).—The tetrahydroquinolinecarboxylic acids containing the carboxy-groups in the benzene nucleus behave towards methyl iodide precisely in the same way as tetrahydroquinoline-5-carboxylic acid, and give rise to the 1-methyl-carboxylic acids, and not to methyl esters.

Tetrahydroquinoline-8-carboxylic acid is readily decomposed by boiling hydrochloric acid, and is therefore most readily produced by reducing quinoline-8-carboxylic acid with tin and hydrochloric acid at temperatures below  $40\text{--}50^\circ$ ; its *nitrosoamine*,  $\text{C}_{10}\text{H}_{10}\text{ON}_2$ , crystallises in yellowish-white, hexagonal plates, and decomposes at  $124^\circ$ .

*Kairolin-8-carboxylic acid*,  $\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}$ , obtained by digesting the potassium salt of the preceding acid with methyl iodide in methyl alcohol at  $100^\circ$ , crystallises from benzene in white needles and melts at  $218\text{--}219^\circ$ . 1-Ethyltetrahydroquinoline-8-carboxylic acid, produced in a similar manner by the action of alcoholic ethyl iodide, crystallises in white plates and melts at  $196\text{--}197^\circ$ .

*Tetrahydroquinoline-7-carboxylic acid*, prepared by reducing quinoline-*m*-carboxylic acid, crystallises from dilute alcohol in white leaflets melting at 189°; its ammonium salt gives white, yellowish-white, pink, and pale green, amorphous precipitates with silver, mercuric, ferric, and cupric salts respectively. Lead acetate gives a white, crystalline, insoluble lead salt, but calcium and barium chlorides do not produce precipitates. The *nitrosoamine* crystallises from benzene in yellowish-white needles and decomposes at 191°.

*Kairoline-7-carboxylic acid* and *1-ethyltetrahydroquinoline-7-carboxylic acid*, the alkylation products of the preceding acid, separate from benzene in prismatic crystals melting respectively at 185° and 163—164°.

*Tetrahydroquinoline-6-carboxylic acid* is obtained by reducing quinoline-6-carboxylic acid, the latter being produced by oxidising 6-methylquinoline; it crystallises in white needles and decomposes at 170°, evolving carbon dioxide; the *nitrosoamine* forms yellowish-white prisms decomposing at 181°; the ammonium salt gives white, yellow, and grey precipitates with silver, lead, and cupric salts; the calcium and barium salts are soluble.

*Kairoline-6-carboxylic acid*, prepared like the methylcarboxy-acids, crystallises from benzene in four-sided prisms melting and decomposing at 224°.

*1-Ethyltetrahydroquinoline-6-carboxylic acid* crystallises from benzene in leaflets and melts at 200° to a red oil.

In all these cases, the products of alkylation are completely soluble in cold dilute solutions of the alkali hydroxides, and hence no alkyl esters are formed.

The alkylated carboxy-acids melt at higher temperatures than the corresponding tetrahydroquinolinecarboxylic acids. G. T. M.

**Acridine Syntheses by Means of *o*-Aminobenzyl Alcohol.**  
By FRITZ ULLMANN and C. BAEZNER (*Ber.*, 1902, 35, 2670—2672).—

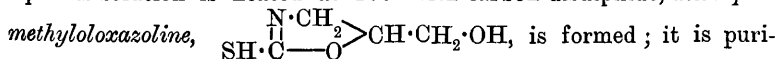
1:2-Phenonaphthacridine,  $C_6H_4 \begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix} C_{10}H_6$ , is prepared by heating together *o*-aminobenzyl alcohol and  $\beta$ -naphthol finally at 200—210°; the substance is isolated in the form of the picrate. It forms pale yellow crystals melting at 131°, and is identical with the compound obtained from formaldehyde, aniline, and  $\beta$ -naphthol; it can also be prepared by melting together *o*-aminobenzyl alcohol and  $\beta$ -naphthylamine, or from *o*-aminobenzyl sulphide and  $\beta$ -naphthol. 3-Diethylaminoacridine,  $C_6H_4 \begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix} C_6H_3 \cdot NEt_2$ , is prepared by heating *o*-aminobenzyl alcohol and diethyl-*m*-aminophenol in carbon dioxide at 210°; the picrate crystallises in orange needles; the solutions of the base are yellow in colour and have a green fluorescence.

K. J. P. O.

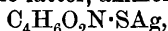
**Action of Carbon Disulphide on Polyhydric Aminoalcohols.**  
By LEON MAQUENNE and E. ROUX (*Compt. rend.*, 1902, 134, 1589—1592).—Polyhydric aminoalcohols react with carbon disulphide



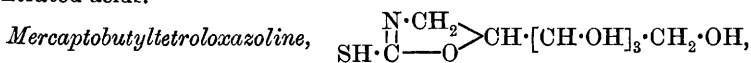
in a manner differing from that of monohydric aminoalcohols (Gabriel, Abstr., 1889, 870, and 1890, 472). When aminopropyleneglycol in aqueous solution is heated at  $100^\circ$  with carbon disulphide, *mercaptop-methylloxazoline*,



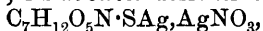
is formed; it is purified by adding silver nitrate to its aqueous solution, when an almost insoluble *silver* derivative,  $\text{C}_4\text{H}_6\text{O}_2\text{N} \cdot \text{S} \cdot \text{Ag} \cdot \text{HNO}_3$ , is precipitated; the latter crystallises in small, colourless plates; excess of silver nitrate produces a *di-silver* derivative,  $\text{C}_4\text{H}_6\text{O}_2\text{N} \cdot \text{S} \cdot \text{Ag} \cdot \text{AgNO}_3$ , which crystallises in slender needles, and is converted by nitric acid into the mono-silver derivative. From the latter, ammonia sets free the base,



which is gelatinous, and converted by hydrogen sulphide into the oxazoline; this substance is a colourless, syrupy oil, very soluble in water, is without taste or smell, and is not attacked by alkalis or concentrated acids.



prepared from glucamine and carbon disulphide at  $100^\circ$ , crystallises in needles melting at  $156^\circ$ ; its *di-silver* derivative,



is formed as a white, crystalline precipitate when silver nitrate is added to its aqueous solution; nitric acid dissolves it, but does not convert it into the mono-silver derivative; the base is obtained as a gelatinous precipitate on treating the silver derivative with ammonia.

K. J. P. O.

**Thiopyronine.** By JOACHIM BIEHRINGER and WASSIL TOPALOFF (*J. pr. Chem.*, 1902, [ii], 65, 499—511. Compare Abstr., 1897, i, 73).

—On treatment of tetramethyldiaminodiphenylmethane with a solution of sulphur in sulphuric acid containing 25 per cent. of sulphur trioxide, dilution with water and addition of zinc chloride, *thiopyronine zinc chloride* crystallises out in red-green, glistening leaflets, which dissolve in water to a red solution with yellow fluorescence; the mother liquor contains unchanged tetramethyldiaminodiphenylmethane along with the corresponding benzhydrol.

On addition of sodium hydroxide to the aqueous solution of the double salt, the *thiopyronine* forms a violet, flocculent precipitate which contains more or less *tetramethyldiaminothioxanthone*. The *thiopyronine* is soluble in warm alcohol, acetone, or chloroform, more sparingly in hot benzene to red solutions with weak yellow fluorescence. On addition of sodium hydroxide to the alcoholic solution, the red colour disappears and is replaced by the blue fluorescence of the thioxanthone. Thiopyronine forms a *hydrochloride*,  $\text{C}_{17}\text{H}_{18}\text{N}_2\text{S} \cdot 2\text{HCl}$ , crystallising in golden-green, glistening needles which melt at  $245^\circ$ , and a *platinichloride*,  $(\text{C}_{17}\text{H}_{18}\text{N}_2\text{S})_2 \cdot \text{H}_2\text{PtCl}_6$ , crystallising in glistening, green needles. The *leuco-base*, formed by reduction with zinc dust and hydrochloric acid, crystallises from dilute alcohol in clusters of colourless needles, melts at  $130^\circ$ , and is easily oxidised to the dye.

Tetramethyldiaminothioxanthone, formed by oxidation of thiopyron-

ine by potassium permanganate in aqueous potassium hydroxide solution, or by warming with aqueous sodium hydroxide, crystallises in yellow prisms, melts at  $288^{\circ}$ , when heated is partially volatile without decomposition, and is easily soluble in hot chloroform, but only sparingly so in hot ethyl acetate, petroleum, benzene, or acetone. The solution in petroleum is colourless, in other solvents yellow; the alcoholic and acetone solutions have a distinct blue fluorescence, the solution in concentrated sulphuric acid has a strong green fluorescence which changes to blue on addition of much alcohol and disappears on addition of water.

The *hydrochloride*,  $C_{17}H_{18}ON_2S \cdot 2HCl \cdot 3\frac{1}{2}H_2O$ , is a stellate, crystalline, reddish-yellow mass, which loses water and hydrogen chloride on warming. The *platinichloride*,  $(C_{17}H_{18}ON_2S)_2 \cdot H_2PtCl_6$ , forms clusters of yellow needles.

The hydrobromide of the *tribromo-derivative*,  $C_{17}H_{15}ON_2SBr_3 \cdot HBr$ , formed by the action of bromine in boiling glacial acetic acid solution, crystallises in plates and melts and decomposes at  $235^{\circ}$ . The tribromo-derivative, precipitated by ammonia from its solution in acetic acid, crystallises from acetone in red leaflets. G. Y.

**Thiosemicarbazide as a Reagent for Aldehydes and Ketones.** By MARTIN FREUND and ALFRED SCHANDER (*Ber.*, 1902, 35, 2602—2606. Compare Neuberg and Neimann, this vol., i, 572, and *Abstr.*, 1897, i, 125, 126).—The following thiosemicarbazones were prepared to illustrate the employment of thiosemicarbazide in the identification and characterisation of aldehydes and ketones; they are obtained by mixing their generators either alone or in acetic acid, alcoholic, or aqueous solutions.

*Acetaldehydethiosemicarbazone*,  $CHMe \cdot N \cdot NH \cdot CS \cdot NH_2$ , separates from water in white crystals and melts at  $146^{\circ}$ .

*Citraldehydethiosemicarbazone* forms white flakes and melts at  $107$ — $108^{\circ}$ .

*Benzaldehydethiosemicarbazone*,  $CHPh \cdot N \cdot NH \cdot CS \cdot NH_2$ , a yellowish-white, crystalline product, sinters at  $155^{\circ}$  and melts at  $160^{\circ}$ .

*Salicylaldehydethiosemicarbazone* forms yellow crystals, sinters at  $215^{\circ}$ , and melts at  $231^{\circ}$ .

*p-Hydroxybenzaldehydethiosemicarbazone* separates from methyl or ethyl alcohol in slender, felted, yellow needles, sintering at  $215^{\circ}$  and melting at  $224^{\circ}$ .

*Cinnamaldehydethiosemicarbazone*, a white, crystalline substance, melts at  $123^{\circ}$ . *Vanillinthiosemicarbazone* separates in slender, yellow needles, sintering at  $194^{\circ}$  and melting at  $196$ — $197^{\circ}$ .

*Acetonethiosemicarbazone*,  $CMe_2 \cdot N \cdot NH \cdot CS \cdot NH_2$ , is a white, crystalline compound sintering at  $174^{\circ}$  and melting at  $179^{\circ}$ .

*Ethyl acetoacetate-thiosemicarbazone*,  $C_6H_{10}O_2 \cdot N \cdot NH \cdot CS \cdot NH_2$ , separates from hot water as an oil which solidifies to a white, crystalline mass; it melts at  $97^{\circ}$ .

*Ethyl succinylsuccinate-bisthiosemicarbazone* is a yellow, crystalline mass insoluble in all the ordinary solvents; it turns brown at  $250^{\circ}$ , but does not melt below  $275^{\circ}$ .

*Diketohexamethylenebisthiosemicarbazone*,  $C_6H_8(\cdot N \cdot NH \cdot CS \cdot NH_2)_2$ , is

an insoluble, white, crystalline mass which darkens and melts at 210—215°. G. T. M.

*p*-Azoxybenzaldehyde. By FRIEDRICH J. ALWAY (*Amer. Chem. J.*, 1902, 28, 34—48).—It has been shown by Gattermann (*Abstr.*, 1897, i, 189) that when *p*-nitrobenzaldehyde is submitted to electrolytic reduction, the *N*-*p*-formylphenyl ether of *p*-nitrobenzaldoxime is produced. If this substance is treated with ferric chloride, a compound is obtained identical with the *p*-azoxybenzaldehyde described by Kirpal (*Abstr.*, 1897, i, 520).

*p*-Azoxybenzaldehyde melts at 190° (not at 194° as stated by Kirpal); it undergoes no change when treated with concentrated sulphuric acid at 100°, and is not affected by concentrated nitric acid, benzoyl chloride, acetyl chloride, or nitrous acid. By the action of zinc dust and acetic acid on the aldehyde, a red, crystalline substance is produced. The phenylhydrazone melts at 228°. *p*-Azoxybenzylideneaniline,  $\text{ON}_2(\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NPh})_2$ , obtained by boiling the aldehyde with excess of aniline, crystallises in large, yellow leaflets and melts at 185—192°. The *nitro*-derivative,  $\text{O} \begin{smallmatrix} \text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CHO} \\ \text{N}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{CHO} \end{smallmatrix}$ , prepared by treating the aldehyde with hot fuming nitric acid, forms yellow needles, melts at 171—172°, and is readily soluble in hot acetic acid. *p*-Azoxybenzylidene chloride,  $\text{ON}_2(\text{C}_6\text{H}_4\cdot\text{CHCl}_2)_2$ , obtained by the action of phosphorus pentachloride on the aldehyde, crystallises in orange-coloured leaflets and melts at 115—116°.

The *phenylhydrazone* of the *N*-*p*-formylphenyl ether of *p*-nitrobenzaldoxime,  $\text{NHPh}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{N} \begin{smallmatrix} \text{O} \\ \text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 \end{smallmatrix}$ , forms dark red leaflets and melts at 222°. When the *N*-*p*-formylphenyl ether of *p*-nitrobenzaldoxime is heated with aniline, the *anilide* of *p*-aldehydohydrazobenzene,  $\text{NHPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NPh}$ , is produced, which crystallises in orange-coloured leaflets and melts at 183—186°.

If *p*-nitrosobenzaldehyde is added to concentrated sulphuric acid, a substance,  $(\text{C}_7\text{H}_5\text{O}_2\text{N})_x$ , is obtained, which forms a dark red powder and melts at 204—206°. By the action of aniline on *p*-nitrosobenzaldehyde, *benzeneazobenzylideneaniline*,  $\text{PhN}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NPh}$ , is produced, which crystallises in small, orange-coloured needles and melts at 125—130°; if this compound is treated with boiling dilute acetic acid, *benzeneazobenzaldehyde*,  $\text{C}_6\text{H}_5\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ , is formed, which crystallises in lustrous, brownish-red leaflets and melts at 116°. The *phenylhydrazone* of benzeneazobenzaldehyde forms long, red needles and melts at 154°.

The *aldehyde*, obtained from *m*-nitrobenzaldehyde by methods analogous to those used in the conversion of *p*-nitrobenzaldehyde into *p*-azoxybenzaldehyde, melts at 129° and yields a *phenylhydrazone* melting at 198°. E. G.

*Dibenzoylhydrazobenzene*. By PAUL FREUNDLER (*Compt. rend.*, 1902, 134, 1509—1510).—Biehringer and Busch (this vol., i, 575) have described dibenzoylhydrazobenzene as a substance melting

at 161°, which, when saponified, gives aniline. *Dibenzoylhydrazobenzene* has been prepared by a method different from that employed by the authors mentioned, but it melts at 138° and is easily saponified with dilute alkali, giving hydrazobenzene.

The compound described by Biehringer and Busch has been identified as benzaniline. J. McC.

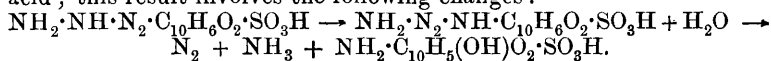
**Replacement of the Diazo-group by Amidogen.** By LEONHARD WACKER (*Ber.*, 1902, 35, 2593—2602).—The *anhydride*,

$C_{14}H_6O_2 \cdot \begin{smallmatrix} N \\ | \\ S \\ | \\ O_3 \end{smallmatrix} \cdot N$ , of 1-diazoanthraquinone-2-sulphonic acid, obtained by

treating 1-aminoanthraquinone-2-sulphonic acid, or 1-hydroxylaminoanthraquinone-2-sulphonic acid, with nitrous acid, is a light yellow, crystalline powder decomposing at 142°. When suspended in water and treated with ammonia or ammonium carbonate, this diazo-compound is reconverted into the original aminosulphonic acid, the reaction being accompanied by an elimination of nitrogen. Other primary amines produce a similar effect, but give rise, in the first place, to intermediate diazoamines. Aniline and the diazoanhydride yield a diazoamino-compound which is isolated in the form of its *potassium* salt,  $NHPh \cdot N_2 \cdot C_{14}H_6O_2 \cdot SO_3K$ , a voluminous, orange-yellow precipitate, which, when boiled with dilute sulphuric acid, evolves nitrogen and becomes decomposed into phenol and the original aminosulphonic acid.

A red diazoamino-compound is formed from the diazoanhydride and methylamine; it is readily decomposed by warm water or dilute acids, also giving rise to the original aminosulphonic acid. These reactions are assumed to be due to the following series of changes,  $NHR \cdot N_2 \cdot C_{10}H_6O_2 \cdot SO_3H \rightarrow R \cdot N_2 \cdot NH \cdot C_{10}H_6O_2 \cdot SO_3H \rightarrow R \cdot OH + N_2 + NH_2 \cdot C_{10}H_6O_2 \cdot SO_3H$ . This assumption is justified by the fact that diethylamine and the diazoanhydride combine to form a diazoamino-compound, which, when heated with dilute acid, decomposes into diethylamine, 1-hydroxyanthraquinone-2-sulphonic acid, and nitrogen. In this case, the initial rearrangement of the diazoamino-compound is not possible.

When hydroxylamine hydrochloride and the diazoanhydride are condensed in the presence of sodium acetate, a *diazohydroxyamide*,  $OH \cdot NH \cdot N_2 \cdot C_{10}H_6O_2 \cdot SO_3Na$ , is produced as a yellowish-brown, amorphous product, which, when warmed with concentrated sulphuric acid at 70°, becomes transformed quantitatively into 1-amino-4-hydroxyanthraquinone-2-sulphonic acid. The potassium salt of the latter acid dissolves in water to a red solution; the acid itself can be diazotised and condensed with hydroxylamine, the product dissolving in water to a pink solution which changes to a greenish-blue colour when rendered alkaline. This reaction serves to identify the aminohydroxy-acid. Hydrazine and the diazoanhydride condense to form a diazohydrazide; this substance, when treated with cold concentrated sulphuric acid, furnishes a good yield of 1-amino-2-hydroxyanthraquinone-2-sulphonic acid; this result involves the following changes:



The aminohydroxy-acid was also identified by conversion into a

quinizarin-green-sulphonic acid by heating with boric acid, stannous chloride, and *p*-toluidine. G. T. M.

**Action of Diazo-salts on Desmotroposantonin and Desmotroposantonous Acid.** By EDGAR WEDEKIND and OSCAR SCHMIDT (*Compt. rend.*, 1902, 135, 43—45).—Santonin does not combine with diazo-salts, but desmotroposantonin combines readily with the diazo-salts of *p*-toluidine, *o*-nitroaniline, *p*-nitroaniline, *p*-aminobenzoic acid, sulphanilic acid, and toluidine, yielding yellow or red crystallisable compounds which melt above 260°.

Desmotroposantonous acid similarly combines with the diazo-derivatives of aniline and *p*-toluidine, forming compounds which melt about 50° lower than the corresponding compounds from desmotroposantonin.

The different behaviour of santonin and desmotroposantonin towards diazo-compounds agrees with Andreocci's view as to their constitution (Abstr., 1894, i, 205). C. H. B.

**New Amino-acid from Gelatin.** By EMIL FISCHER (*Ber.*, 1902, 35, 2660—2665).—Hydroxyamino-acids are present in the hydrolytic products of proteids, gelatin, &c. A new hydroxyamino-acid can be isolated from the mother liquor from which the esters of the mono-amino-acids have been extracted (see this vol., i, 512) in the hydrolysis of gelatin. The thick mother liquor is dissolved in water, acidified, and slowly evaporated; during the evaporation, the inorganic salts partly separate; the syrupy mother liquor is repeatedly treated with alcoholic hydrogen chloride and evaporated in vacuum to remove monoamino-acids. The residue, which consists only of salts, diamino-acids, and hydroxyamino-acids is dissolved in water, saturated with hydrogen chloride, evaporated, and treated with alcoholic hydrogen chloride; the inorganic salts are thus completely removed. From the aqueous solution of the residue, the hydroxyamino-acid can be precipitated by phosphotungstic acid. From 1 kilogram of gelatin, 30 grams of crude crystallised product were obtained. The acid,  $C_5H_9O_3N$ , crystallises in colourless plates belonging to the rhombic system [ $a : b : c = 0.59405 : 1 : 0.3579$ ], and has  $[\alpha]_D - 81.04^\circ$  at 20°; when heated, the acid decomposes at 270°, and gives off vapour containing pyrrole. The copper salt forms deep blue, very soluble crystals. With phenylcarbimide, it forms a compound,  $C_{12}H_{14}O_4N_2$ , which crystallises in colourless leaflets melting and decomposing at 175°. On reducing the hydroxyamino-acid with phosphorus and hydriodic acid, *r*-2-pyrrolidinecarboxylic acid is obtained. The new acid is therefore a hydroxypyrrolidine-2-carboxylic acid.

A description is given of the taste of the various classes of amino-acids. K. J. P. O.

**Basic Products of the Profound Hydrolysis of Muscle.** By ALEXANDRE ÉTARD (*Bull. Soc. Chim.*, 1902, [iii], 27, 693—696).—From calf's muscle macerated in sulphuric acid and heated with this in a reflux apparatus, the author obtained leucine, tyrosine, glycine, and glutamic acid. Other basic substances, for example, one similar to lysine carbonate, have been obtained, but not in a condition suitable for analysis. A. F.

**Certain Chemical and Physical Properties of Hæmoglobin.** By ARTHUR GAMGEE (*Proc. Roy. Soc.*, 1902, 70, 79—83).—Solutions containing oxyhæmoglobin of great purity and in varying concentration were prepared, and photographs of the cadmium spark spectrum, with and without the interposition of the solutions, were obtained. There are no absorption bands corresponding with either the 14th or 17th cadmium line, and the band observed by Soret corresponding with the 14th is therefore due, not to the blood colouring matter, but to some other constituent.

The author's investigations show that the conductivity of oxyhæmoglobin solutions is low, but very much higher than that found by Stewart at 5°. The conductivity increases rapidly with rising temperature, and undergoes permanent changes when the solutions are kept for even a short time above 0°.

When oxyhæmoglobin solutions are electrolysed, the anode and cathode being separated by an animal membrane, there is first of all a separation of colloidal hæmoglobin in the anode compartment, and then a rapid and complete transport of the same to the cathode compartment. The author considers this process to be of a similar nature to the phenomena of electro-endosmose, studied by Quincke. What has been said with regard to oxyhæmoglobin applies also to carbon monoxide hæmoglobin.

Evidence is brought forward to prove that the precipitated colloidal, and yet perfectly soluble, hæmoglobin represents the undecomposed molecule of the blood colouring matter. The readiness with which this colloidal hæmoglobin passes through animal membranes under the conditions just mentioned suggests that certain absorption phenomena in the animal body may be intimately connected with electromotive changes in the tissues.

J. C. P.

**Action of Phosphorus Pentachloride on Aniline.** By J. ELLIOTT GILPIN (*Amer. Chem. J.*, 1902, 27, 444—454. Compare *Abstr.*, 1897, i, 463).—When a cold saturated solution of phosphorus pentachloride in benzene is added slowly to a benzene solution of aniline and the mixture left for some time, aniline hydrochloride separates. When the benzene is distilled off and the residue washed with boiling water and crystallised from hot alcohol, the compound,  $\text{P}(\text{NPh})_2 \cdot \text{NHPh}$ , separates in well-defined, rhombic crystals [ $a:b:c:0.27956:1:0.258614$ ], which melt at 208—210°. The substance is not acted on by water or alcoholic potassium hydroxide, but is decomposed by concentrated sulphuric acid or concentrated nitric acid.

When aniline acts on phosphorus pentachloride at a high temperature the compound,  $\text{P}_2\text{Cl}(\text{NHPh})_7$ , is formed as a bye-product, and is extracted from the mixture by means of a small quantity of alcohol. It crystallises with 2 mols. of alcohol in monoclinic crystals [ $a:b:c:1.32375:1:0.55845$ ], and exhibits a hemihedral habit. It melts at 192—194°.

J. McC.

## Organic Chemistry.

**Direct Hydrogenation of Acetylene Hydrocarbons by Contact Action.** By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1902, 135, 87—89).—Heptylidene, in presence of excess of hydrogen and in contact with reduced nickel at about  $170^{\circ}$ , is converted into normal heptane together with small quantities of higher hydrocarbons of the same series. Reduced copper above  $200^{\circ}$  produces  $\alpha$ -heptylene, diheptylene, and triheptylene as well as normal heptane. Phenylacetylene, in presence of excess of hydrogen, is converted by nickel at about  $180^{\circ}$  into ethylcyclohexane boiling at  $130^{\circ}$  together with a small quantity of methylcyclohexane. Copper at  $190^{\circ}$  to  $250^{\circ}$  converts the phenylacetylene mainly into metastyrene, ethylbenzene, and diphenylbutane, the yield of the last reaching as much as 50 per cent. (compare this vol., i, 525). C. H. B.

**Reduction of Nitro-compounds by Direct Hydrogenation in Contact with Finely Divided Metals.** By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1902, 135, 225—227. Compare Abstr., 1901, i, 459).— $\alpha$ -Nitronaphthalene with an excess of hydrogen, when in contact with finely divided copper at  $330$ — $350^{\circ}$ , is reduced to  $\alpha$ -naphthylamine. The reduction can also be carried out with a mixture of carbon monoxide and hydrogen. With nickel at the same temperature, the reduction proceeds further, so that some tetrahydronaphthalene is produced.

In presence of reduced nickel at  $150$ — $180^{\circ}$ , nitromethane is completely reduced to methylamine, but at  $320^{\circ}$  reduction takes place to methane and ammonia. Nitromethane is not reduced by hydrogen in presence of copper below  $300^{\circ}$ ; above this temperature, reaction takes place, part of the nitromethane suffers reduction, and a compound of nitromethane with methylamine results, the product being identical with a solution of nitromethane in aqueous methylamine.

With nickel at  $200^{\circ}$ , nitroethane is easily reduced to ethylamine. The reaction with copper is analogous to that found for nitromethane. J. McC.

**Action of Hydrazine Hydrate on the Aldol from *iso*Butyraldehyde and Formaldehyde.** By BERTHOLD KÖNIG (*Monatsh.*, 1902, 23, 469—478. Compare Abstr., 1900, i, 212, 428).— $\gamma$ -Hydroxy- $\beta\beta$ -dimethylpropionaldazine,  $(\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CH})_2\text{N}_2$ , formed by the action of hydrazine hydrate on the aldol obtained from *iso*-butyraldehyde and formaldehyde, crystallises in colourless masses, melts at  $151^{\circ}$ , boils and decomposes at  $190^{\circ}$  under atmospheric pressure, at  $165^{\circ}$  under 25 mm. pressure, is easily soluble in acetone, alcohol, ether, benzene, chloroform, or water, but only sparingly so in carbon disulphide or light petroleum, and gives the pyrazoline reactions with potassium permanganate or with wood-fibre in dilute hydrochloric acid (Abstr., 1895, i, 248).

Cryoscopic and ebullioscopic molecular weight determinations indicate

the formula  $C_{10}H_{20}O_2N_2$ . When distilled or when exposed to moist air containing acid vapours, the aldazine is decomposed, giving an odour of amines and of ammonia.

When heated with dilute sulphuric acid at  $90^\circ$ , boiled with dilute aqueous or alcoholic hydrochloric acid, or when treated with hydrogen chloride in benzene solution, the aldazine is hydrolysed to hydrazine and the aldol.

When heated with maleic acid at  $130^\circ$ , the aldazine forms a yellow, crystalline *derivative* which melts at  $121^\circ$ , decomposes at  $150^\circ$ , and is probably a pyrazoline compound.

G. Y.

**Sulphur and Nitrogen Derivatives of Carbon Disulphide.**  
**V. Dithiocarbamic Esters derived from Secondary Aromatic Amines.** VI. Aromatic Iminodithiocarbamic Esters. By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1902, [iii], 27, 807—812. Compare Abstr., 1901, i, 518; this vol., i, 199, 353, 595, 597).—By the action of carbon disulphide on methylaniline in presence of an alcoholic solution of ammonia, the author obtained *ammonium methylphenyldithiocarbamate*,  $NMePh \cdot CS \cdot SNH_4$ , in the form of yellowish, lozenge-shaped plates, sparingly soluble in cold water or alcohol, and insoluble in ether; it is only slightly stable in air. *Ammonium phenylethyldithiocarbamate*, obtained in a similar manner, is closely analogous in its properties to the preceding compound. Dithiocarbamic esters can be readily prepared by acting with an alkyl haloid on the preceding salts suspended in cold alcohol.

By acting on a dithiocarbamic ester derived from aniline in cold ethereal solution with methyl iodide, the hydriodide of an iminodithiocarbamic ester is obtained which decomposes in aqueous solution into the ester and hydriodic acid. On employing an alcoholic solution and heating at  $50$ — $70^\circ$ , the ester is also formed, but the reaction is more complicated. Quantitative yields are obtained by acting with an alkyl iodide on dithiocarbamates dissolved in alcoholic solutions of potassium hydroxide. *Methyl phenyliminodithiocarbonate*,  $NPh \cdot C(SMe)_2$ , boils at  $300^\circ$ , solidifies on cooling, and crystallises from alcohol in elongated prisms which melt at  $36^\circ$ . The *hydriodide* melts between  $110^\circ$  and  $120^\circ$  and froths at about  $130^\circ$ . The *picrate* is viscous and is decomposed by water. *Methyl p-tolyliminodithiocarbonate*,  $C_6H_4Me \cdot N \cdot C(SMe)_2$ , boils at  $315^\circ$ .

A. F.

**Sulphur and Nitrogen Derivatives of Carbon Disulphide.**  
**VII. Dithiocarbamic Esters derived from Primary Amines.** By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1902, [iii], 27, 812—818. Compare preceding abstract).—These are best prepared by acting on the sulphocarbamic derivatives of primary amines with 1 mol. of an alkyl haloid. In this way, the author has prepared *methyl methyldithiocarbamate*,  $NHMe \cdot CS \cdot SMe$ , a thick, heavy, refractive liquid which crystallises in methyl chloride; *ethyl methyldithiocarbamate*, an oily liquid; *benzyl methyldithiocarbamate*, which crystallises in small plates melting at  $49.5^\circ$ ; and *benzyl phenyldithiocarbamate*.

On being heated, these compounds all decompose into thiocarbimide and mercaptan. When heated with ammonia or with amines, they also undergo decomposition with formation of substituted thiocarbamides



and mercaptan, a reaction which constitutes a new method of synthesis of mono-, di-, *s*-, and tri-substituted thiocarbamides. The dithiocarbamic esters derived from primary amines also combine with a second mol. of an alkyl haloid, yielding symmetrical or mixed iminodithiocarbonic esters. When subjected to the action of ferric chloride, those dithiocarbamates in which a fatty radicle is attached to nitrogen are un-attacked, whilst those in which an aromatic radicle is attached to nitrogen give rise to *isothiuram disulphides*; the compound  $\text{NPh}\cdot\text{C}(\text{SMe})\cdot\text{S}\cdot\text{S}(\text{SMe})\cdot\text{C}\cdot\text{NPh}$  forms colourless needles melting at  $123^\circ$ , and the compound

$\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{C}(\text{SMe})\cdot\text{S}\cdot\text{S}(\text{SMe})\cdot\text{C}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$  [Me : N = 1 : 4] forms colourless needles melting at  $158^\circ$ .

To explain the difference in the behaviour of the primary dithiocarbamates, the author, as also for other reasons, considers that the two classes of compounds differ in constitution, those derived from fatty amines having their hydrogen attached to nitrogen, whereas in the compounds derived from aromatic amines, the hydrogen is attached to sulphur.

A. F.

**Action of Organic Acids on Metallic Antimony. I.** By B. MORITZ and C. SCHNEIDER (*Zeit. physikal. Chem.*, 1902, **41**, 129—138).—When powdered antimony is shaken with solutions of certain organic acids in the presence of air, the antimony is attacked. The presence of air is essential, and the diminution of the air volume accompanying the action corresponds with the quantity of oxygen it contains and with the quantity of antimony which has passed into solution. Only acids containing the hydroxyl as well as the carboxyl group have the power of attacking antimony under the above conditions; further, it appears that the hydroxyl and carboxyl groups must be attached to the same carbon atom; thus, whilst  $\alpha$ -hydroxybutyric acid acts readily on the metal, the  $\beta$ -acid is almost without effect. In all cases, the quantity of antimony passing into solution is greatest when the acid has been partly neutralised with soda, and the mixture therefore contains the acid salt. Of dibasic acids, oxalic, malic, tartaric, and citric acids readily attack antimony as above described. Malonic and succinic acids, on the other hand, are without effect, and the same holds for phenol and benzoic and salicylic acids. Solutions of gallic and tannic acids produce in a few minutes precipitates containing antimony.

In the course of their work, the authors have isolated a crystalline compound of lactic acid with sodium and antimony, having the empirical formula  $\text{SbONa}_2(\text{C}_3\text{H}_5\text{O}_3)_3$ .

J. C. P.

**Mercury Lactates.** By MARCEL GUERBET (*Bull. Soc. Chim.*, 1902, [iii], **27**, 803—807).—The author has prepared mercurous lactate by dissolving freshly precipitated mercurous oxide in dilute lactic acid, previously heated with water in order to destroy the anhydride, &c., which it contains. The solution thus obtained is allowed to evaporate in a desiccator over sulphuric acid, when mercurous lactate separates out in short, white, prismatic needles having the composition  $(\text{C}_3\text{H}_5\text{O}_3)_2\text{Hg}_2\cdot\text{H}_2\text{O}$ . It does not dissolve entirely in water, hydrolysis occurring with formation of a basic lactate, which then decomposes into mercuric lactate and mercury.

In a similar manner, by dissolving yellow mercuric oxide in dilute lactic acid and allowing the solution to evaporate over sulphuric acid, mercuric lactate separates out in colourless prismatic needles having the composition  $(C_3H_5O_3)_2Hg$ . It is very soluble in water; on boiling this solution, the mercuric salt passes into mercurous, and there are formed at the same time carbon dioxide, aldehyde, and lactic acid.

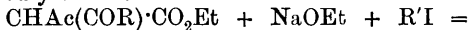
The substances described as lactates of mercury by Engelhard and Maddrel and by Brüning are found by the author to be mixtures.

A. F.

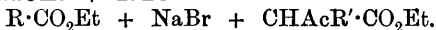
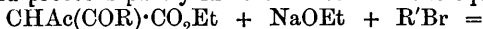
**Action of Nitrous Acid on  $\alpha$ -Substituted  $\beta$ -Ketonic Esters. Synthesis of the Homologues of Pyruvic Acid.** By LOUIS BOUVEAULT and RENÉ LOCQUIN (*Compt. rend.*, 1902, 135, 179—182).—By the action of nitrous acid on  $\alpha$ -substituted acetoacetates, two products are formed according to the equations: (I)  $COMe \cdot CHR \cdot CO_2Et + HNO_2 = Me \cdot CO_2H + NOH \cdot CR \cdot CO_2Et$  and (II)  $COMe \cdot CHR \cdot CO_2Et + HNO_2 = EtOH + COMe \cdot CR \cdot NOH + CO_2$ . In acid solution, the former reaction takes place exclusively. The same oximoglyoxylic ester is obtained in starting with ethyl ethylhexoylacetate or ethyl ethylacetoacetate, namely,  $NOH \cdot Cet \cdot CO_2Et$ . This *oxime of ethyl methylpyruvate* boils at 125—130° under 10 mm. pressure; it crystallises in white needles which are soluble in light petroleum and melt at 58°. From ethyl isoamylacetylacetate, the authors have prepared the *oxime* of *ethyl isobutylpyruvate*,  $CHMe_2 \cdot [CH_2]_2 \cdot C(\cdot NOH) \cdot CO_2Et$ , as an oil which boils at 114° under 12 mm. pressure and has a sp. gr. 0.9114 at 4°/0°. The corresponding acid, obtained by saponification, melts at 160° with decomposition. *Ethyl isobutylpyruvate* boils at 105° under 18 mm. pressure. Starting with ethyl sec.octylacetoacetate, the *oxime* of *ethyl methylhexylpyruvate*,  $CH_2Me \cdot [CH_2]_4 \cdot CHMe \cdot C(\cdot NOH) \cdot CO_2Et$ , has been obtained as an oil which boils at 177° under 16 mm. pressure and has a sp. gr. 0.9859 at 4°/0°. The corresponding acid melts at 88—89°.

J. McC.

**Preparation of  $\alpha$ -Derivatives of  $\beta$ -Ketonic Esters.** By RENÉ LOCQUIN (*Compt. rend.*, 1902, 135, 108—110).—When the C-esters of the acylacetoacetates (Abstr., 1901, i, 311) are treated with an alkyl iodide and a sodium alkylxide in presence of an excess of alcohol, a good yield is obtained in accordance with the equation



whilst if an alkyl bromide is used the reaction is more complicated and proceeds partly in accordance with the equation



*Ethyl ethylhexoylacetate*, boiling at 128—129° under 13 mm. pressure, and of sp. gr. 0.9325 at 4°/0°, is obtained in this way from *ethyl C-hexoylacetate*, which boils at 136° under 10 mm. pressure and has a sp. gr. 1.032 at 0°. The corresponding 4-ethyl-3-amyl pyrazolone melts at 136°. The action of ethyl bromide on ethyl C-butyrylacetate yields a mixture of ethyl ethylacetoacetate and *ethyl ethyl-*

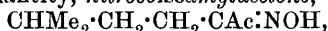
*butyrylacetate* which cannot be separated by fractionation, but *3-methyl-4-ethyl pyrazolone* corresponding with the former melts at  $190^{\circ}$ , whilst *4-ethyl-3-propylpyrazolone* corresponding with the latter melts at  $145^{\circ}$  and is more soluble in alcohol or ether. *Ethyl hexylbutyrylacetate*,  $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{CHMe}\cdot[\text{CH}_2]_5\cdot\text{Me})\cdot\text{CO}_2\text{Et}$ , obtained by the action of secondary octyl iodide on ethyl C-butyrylacetate, boils at  $166^{\circ}$  under 16 mm. pressure and has a sp. gr.  $0.9347$  at  $4^{\circ}/0^{\circ}$ . Its pyrazolone is liquid and boils and partially decomposes at about  $270^{\circ}$  under 30 mm. pressure.

C. H. B.

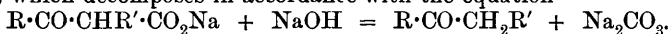
**Di-*p*-phenetide of Agaric Acid.** J. D. RIEDEL (D.R.-P. 130073).—The *di-p-phenetide* of agaric acid, produced by heating this acid with 2.5 mols. of *p*-phenetidine at  $140$ — $160^{\circ}$  either under pressure or in a current of indifferent gas, crystallises from glacial acetic acid, alcohol, or a mixture of benzene and petroleum in small needles melting at  $150$ — $151^{\circ}$ ; it is insoluble in water or dilute acid or alkaline solutions. The compound is very soluble in cold chloroform, but dissolves less readily in other organic solvents of low boiling point.

G. T. M.

**Action of Alkali Nitrites on  $\alpha$ -Substituted  $\beta$ -Ketonic Esters.** By LOUIS BOUVEAULT and RENÉ LOCQUIN (*Compt. rend.*, 1902, 135, 295—297).—When ethyl *isoamylacetate* is treated successively with an alkali hydroxide, sodium nitrite, and an acid, it yields, in almost calculated quantity, *nitrosoisoamylacetone*,



which melts at  $32$ — $33^{\circ}$ , boils at  $128^{\circ}$  under 18 mm. pressure and with hydroxylamine yields a dioxime melting at  $181^{\circ}$ . With the higher homologues of the ester, however, the reaction does not succeed, because the action of the alkali hydroxide yields a very unstable salt, which decomposes in accordance with the equation

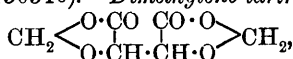


If, however, the ester is mixed with the calculated quantity of sodium ethoxide in presence of absolute alcohol and dry ethyl nitrite is passed into the solution, the reaction proceeds as in an acid solution (this vol., i, 704),  $\text{CHAc}(\text{C}_5\text{H}_{11})\cdot\text{CO}_2\text{Et} + \text{EtNO}_2 = \text{Me}\cdot\text{CO}_2\text{Et} + \text{NOH}\cdot\text{C}(\text{C}_5\text{H}_{11})\cdot\text{CO}_2\text{Et}$ . If amyl nitrite is used instead of ethyl nitrite, mixed esters are obtained by partial substitution of amyl for ethyl.

The results indicate that if the reaction of nitrous acid with the  $\alpha$ -substituted- $\beta$ -ketonic esters takes place under such conditions that the alkyl group is not hydrolysed at all or is hydrolysed in presence of an acid, the products are an acid and the oxime of a substituted glyoxylic ester, whilst if during the reaction the alkyl group is hydrolysed so as to form a salt,  $\text{R}\cdot\text{CO}\cdot\text{CHR}'\cdot\text{CO}_2\text{M}$ , the products are carbon dioxide and the monoxime of an  $\alpha$ -diketone.

C. H. B.

**Dimethylene Tartrate.** CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 130346).—*Dimethylene tartrate*,

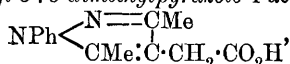


produced by heating tartaric acid with paraformaldehyde or trioxo-

methylene at 140—150° and treating the clear solution thus obtained with concentrated sulphuric acid at 60°, crystallises from alcohol, acetone, or chloroform in needles, melts at 120°, and boils without decomposition at 296°. It is slowly hydrolysed by water and more readily attacked by solutions of the alkali hydroxides and carbonates. The substance may also be obtained by adding to an aqueous solution of tartaric acid and formaldehyde sufficient sulphuric acid or phosphoric acid to combine with the whole of the water. Hydrochloric acid does not induce this condensation.

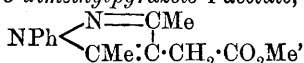
G. T. M.

**Action of Halogen Esters and Ketones on Sodioacetylacetone.** By FR. MARCH (*Ann. Chim. Phys.*, 1902, [vii], 26, 295—366. Compare Abstr., 1900, i, 374; 1901, i, 312, 596, and this vol., i, 484).—1-Phenyl-3:5-dimethylpyrazole-4-acetic acid,



produced by hydrolysing the corresponding ethyl ester with concentrated sodium hydroxide solution, separates from ether in colourless crystals melting at 140—141°; its copper salt,  $\text{Cu}(\text{C}_{13}\text{H}_{13}\text{O}_2\text{N}_2)_2$ , is a violet compound.

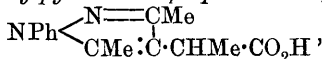
Methyl 1-phenyl-3:5-dimethylpyrazole-4-acetate,



resulting from the interaction of methyl  $\beta\beta$ -diacetylpropionate, phenylhydrazine hydrochloride, and sodium acetate in dilute methyl alcohol, crystallises from ether in prisms melting at 65°; it is insoluble in water, but readily dissolves in methyl or ethyl alcohol, and yields the preceding acid on hydrolysis.

Ethyl  $\beta\beta$ -diacetyl- $\alpha$ -methylpropionate,  $\text{CHAc}_2 \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$ , prepared by heating at 120—140° ethyl  $\alpha$ -bromopropionate and sodioacetylacetone, is an almost colourless oil boiling at 128—130° under 10 mm., and at 149—151° under 33 mm. pressure; it has a sp. gr. 1.067 at 15°, and develops a coloration with ferric chloride; its copper derivative,  $(\text{C}_{10}\text{H}_{15}\text{O}_4)_2\text{Cu}$ , is unstable. The ester, when treated with sodium ethoxide, is hydrolysed into sodium acetate and ethyl  $\alpha$ -methyl-lævulate; the action of sodium hydroxide on the ester gives rise to sodium  $\alpha$ -methyl-lævulate.

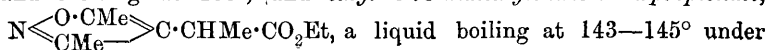
1-Phenyl-3:5-dimethylpyrazole-4- $\alpha$ -propionic acid,



produced by hydrolysing the oily condensation product of the interaction of the preceding ester and phenylhydrazine crystallises from alcohol and melts at 129—130°.

The disemicarbazone of ethyl  $\alpha$ -methyl- $\beta\beta$ -diacetylpropionate is a white, crystalline compound melting at 207—208°.

The action of hydroxylamine on the ester gives rise to two products, the dioxime,  $(\text{NOH} \cdot \text{CMe})_2\text{CH} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$ , crystallising in needles and melting at 133°, and ethyl 3:5-dimethylloxazole-4- $\alpha$ -propionate,

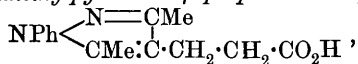


21 mm. pressure; the corresponding *acid*, readily obtained by alkali hydrolysis, forms colourless crystals melting at  $106^{\circ}$ ; its *copper* salt,  $(C_8H_{10}O_3N_2)_2Cu$ , is a light green, insoluble substance melting at  $154-155^{\circ}$ . When the condensation with hydroxylamine is effected by boiling the ester with excess of this reagent and potassium carbonate, another *compound* is formed which probably has the formula  $NOH:CMe \cdot CH \begin{smallmatrix} \text{CHMe} \cdot CO \\ \text{CMe} = N \end{smallmatrix} > O$ ; this product crystallises in needles and melts at  $202-204^{\circ}$ .

*Methyl  $\gamma\gamma$ -diacetylbutyrate*,  $CHAc_2 \cdot CH_2 \cdot CH_2 \cdot CO_2Me$ , a pale yellow liquid boiling at  $160-161^{\circ}$  under 24 mm. pressure, is produced by condensing methyl  $\beta$ -chloropropionate with sodioacetylacetone; it readily dissolves in dilute sodium carbonate solution and develops a red coloration with ferric chloride; the silky, green, *copper* derivative is insoluble in water, alcohol, or ether, but readily dissolves in chloroform; it melts at  $220^{\circ}$ .

*Ethyl  $\gamma\gamma$ -diacetylbutyrate* boils at  $154-155^{\circ}$  under 15 mm. pressure, develops a coloration with ferric chloride, and yields a silky, green, *copper* derivative dissolving in chloroform and melting at  $209^{\circ}$ ; when treated with alkali hydroxides, this ester gives rise to  $\gamma$ -acetylbutyric acid. By the action of sodium ethoxide and methyl iodide, the ester loses an acetyl group and furnishes *ethyl  $\gamma$ -acetyl- $\gamma$ -methylbutyrate*,  $CHMeAc \cdot CH_2 \cdot CH_2 \cdot CO_2Et$ , a pale yellow liquid boiling at  $117-118^{\circ}$  under 23 mm. pressure and having a sp. gr. 1.004 at  $0^{\circ}/0^{\circ}$ ; the corresponding *acid* boils at  $168-169^{\circ}$  under 22 mm. pressure and has a sp. gr. 1.114 at  $0^{\circ}/0^{\circ}$ ; its *semicarbazone*,  $C_8H_{15}O_3N_3$ , melts indefinitely at  $152-158^{\circ}$ .

1-Phenyl-3 : 5-dimethylpyrazole-4- $\beta$ -propionic acid,



produced by condensing ethyl  $\gamma\gamma$ -diacetylbutyrate with phenylhydrazine and hydrolysing the oily product with potassium hydroxide, crystallises from dilute alcohol, &c., in colourless needles and melts at  $134-135^{\circ}$ . The *dioxime*,  $(NOH:CMe)_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot CO_2Et$ , and

*ethyl 3 : 5-dimethylloxazole-4- $\beta$ -propionate*,  $N \begin{smallmatrix} O - CMe \\ \text{CMe} : C \cdot CH_2 \cdot CH_2 \cdot CO_2Et \end{smallmatrix}$

are produced by the action of hydroxylamine on ethyl diacetylbutyrate; the former crystallises in colourless prisms melting at  $108-110^{\circ}$ , the latter is an oil boiling at  $157-158^{\circ}$  under 23 mm. pressure and yielding on hydrolysis the corresponding acid melting at  $109-110^{\circ}$ . The ester, when condensed with semicarbazide, gives rise to the

*compound*  $N \begin{smallmatrix} CMe - C \cdot CH_2 \cdot CH_2 \cdot CO_2Et \\ N(CO \cdot NH_2) : CMe \end{smallmatrix}$ , which melts at

$114-115^{\circ}$ . Ethyl bromoisobutyrate, unlike its lower homologues, does not react with sodioacetylacetone.

*Acetonylacetylacetone*,  $CHAc_2 \cdot CH_2 \cdot Ac$ , produced by condensing chloroacetone and sodioacetylacetone, boils at  $156^{\circ}$  under 35 mm. pressure; its *copper* derivative crystallises from chloroform in needles melting at  $267-268^{\circ}$  and is somewhat volatile.

G. T. M.

**Coloured Organic Ferric Compounds.** By ARTHUR HANTZSCH and CECIL H. DESCH (*Annalen*, 1902, 323, 1—31).—Determinations of the electrical conductivity of aqueous solutions of ferric acetylacetone indicate that the substance is practically a non-electrolyte, the values obtained being  $\epsilon_{256} = 0.72$ , and  $\epsilon_{1024} = 1.68$ . The compound is very slowly decomposed by hydrochloric acid, even when this reagent is in excess, and the change has been studied quantitatively by determining the electrical conductivities of solutions of the substance with one, two, or three molecular proportions of the acid.

The decomposition of the salt by hydrogen chloride in anhydrous solvents is instantaneous and complete, but when the reagent is gradually added the change is seen to occur in three stages, the light red solution becoming deep red, then reddish-violet, and finally assuming the pale yellow colour of ferric chloride. The colour changes correspond with the gradual transformation of  $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$  into  $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}$  and  $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)\text{Cl}_2$ .

Aluminium acetylacetone is as poor a conductor of electricity as its ferric analogue, and is even less readily attacked by hydrochloric acid. *Ethyl ferribenzoylacetate*,  $\text{Fe}(\text{C}_{11}\text{H}_{11}\text{O}_3)_3$ , obtained as an oily residue by extracting with ether a concentrated solution of ferric chloride, sodium acetate, and ethyl benzoylacetate in dilute alcohol, slowly becomes solid and separates from its alcoholic solution in deep red crystals melting at  $128^\circ$ . *Ethyl ferrioxaloacetate*,  $\text{Fe}(\text{C}_8\text{H}_{11}\text{O}_5)_3$ , prepared in a similar manner, separates as a lustrous, dark red, hygroscopic powder on diluting its alcoholic solution with water.

Although ferric chloride and ethyl acetoacetate develop an intense coloration, the amount of ethyl ferriacetoacetate actually produced in aqueous solutions is but very small; the reaction takes place, however, to a greater extent when the reagents are dissolved in alcohol.

*Ferrisalicylic acid*,  $\text{OH}\cdot\text{Fe}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$ , produced by shaking an ethereal solution of salicylic acid with a concentrated aqueous solution of ferric chloride and sodium acetate, crystallises from the ethereal extract in red prisms which contain 1 mol. of ether. The compound, when freed from ether, has a purple colour and dissolves in water to a reddish-violet solution; it behaves as an acid salt, dissolving in solutions of the alkali hydroxides without decomposition.

*o*-Methoxybenzoic acid does not react with ferric chloride; methyl salicylate and salicylaldehyde develop colorations with ferric chloride, but the products could not be isolated. Electrolytic determinations show that the amount of coloured salt formed from phenol and ferric chloride is very small; this is also true of resorcinol, but its isomerides show more tendency to enter into reaction, the amount of double decomposition being greatest in the case of catechol.

Pyrogallol and *p*-aminophenol, when treated with ferric acetate, yield violet-black substances which are insoluble in water or the organic solvents, but dissolve in hydrochloric acid to a yellow solution. Ethyl dicarboxyglutaconate and excess of ferric chloride in dilute alcoholic solution develop a blue coloration, but the actual amount of double decomposition is very small.

*Ferric acetylhydroxamate*,  $\text{Fe}(\text{C}_2\text{H}_4\text{O}_2\text{N})_3$ , separates in deep red prisms

from an alcoholic solution of acetylhydroxamic acid and ferric ethoxide; it readily dissolves in water to a bluish-red solution; its equivalent conductivities at 25° are  $\epsilon_{100.8} = 7.5$ , and  $\epsilon_{201.6} = 8.4$  respectively. The salt is accordingly a "half-electrolyte"; its degree of ionisation, although far less than that of a normal salt, is greatly in excess of that of ferric acetylacetone. The aqueous solution of the salt gives no precipitate with potassium ferrocyanide, but ferric hydroxide is slowly deposited on adding strong ammonia solution; hydrochloric acid develops an intense violet coloration, which disappears on adding excess of the reagent.

*Ferric oxalodihydroxamate*,  $\text{OH} \cdot \text{Fe} \begin{smallmatrix} \text{O} \cdot \text{C} \cdot \text{NOH} \\ | \\ \text{O} \cdot \text{C} \cdot \text{NOH} \end{smallmatrix}$ , produced by the interaction of oxalodihydroxamic acid and ferric acetate, separates as a deep violet precipitate, dissolving in excess of ferric chloride solution to a violet solution. The ferric salt is insoluble in water, alcohol, or ether, explodes on heating, and dissolves in solutions of the alkali hydroxides without decomposition.

*Ferric salicylhydroxamate*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C}(\text{NOH}) \cdot \text{O} \end{smallmatrix} \text{Fe} \cdot \text{OH}$ , resembles the preceding salt and dissolves without decomposition in solutions of the alkali hydroxides.

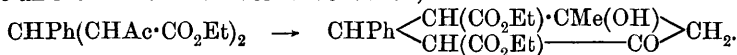
*Lanthanum acetylacetone*,  $\text{La}(\text{C}_5\text{H}_7\text{O}_2)_3$ , is prepared by dissolving freshly precipitated lanthanum oxide in a dilute alcoholic solution of acetylacetone; the reaction is accompanied by development of heat, and the salt crystallises, on cooling, in white needles. In solution, the sparingly soluble lanthanum salt is more highly ionised than its ferric and aluminium analogues; it is more rapidly attacked by hydrochloric acid than these substances.

Acetylacetone and catechol show a slight tendency to interact with boric acid.

Solutions of colloidal ferric hydroxychloride, which have a marked acid reaction and a noteworthy electrical conductivity, contain their chlorine in a non-ionised condition, so that it is not precipitated as silver chloride until after acidifying. It must therefore be supposed that this chlorine exists in these solutions in the form of a complex chloroferric acid. Chlorine exists in a similar condition in the coagula obtained by carefully adding ammonia to aqueous solutions of aluminium chloride until the turbidity produced remains undissolved.

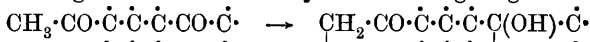
G. T. M.

**8-(1:5)-Diketones.** By PAUL RABE and FRITZ ELZE (*Annalen*, 1902, 323, 83—112).—The 8- or 1:5-diketones containing a methyl group attached to one of their carbonyl radicles readily undergo rearrangement into *cyclohexanolones*. For example, diethyl benzylidene-bisacetoacetate, a condensation product from benzaldehyde and ethyl acetoacetate, gives the reactions of diethyl 3-methyl-5-phenyl-*cyclohexan-3-ol-1-one-4:6*-dicarboxylate, the transformation being due to an intramolecular aldol condensation,



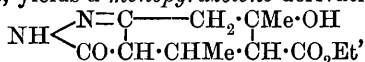
In some cases, this change is complete, in others, the two isomerides

exist together in a condition of equilibrium. Evidence of the inverse transformation is furnished by Knoevenagel's researches (Abstr., 1899, i, 214). The formation of the cyclic isomeride is brought about by the action of piperidine, sodium ethoxide, or other compounds of a similar nature. The  $\delta$ -diketones, which have undergone complete rearrangement, are tabulated and their appropriate designations as cyclic compounds are indicated. The nature of the change involved in this rearrangement is indicated by the following diagram.



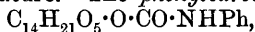
Diethyl methylenebisacetoacetate, when treated with hydrazine hydrate in alcoholic solution, yields 4-methylenebis-3-methyl-5-pyrazolone,  $\text{CH}_2(\text{CH} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CMe} \end{smallmatrix} \text{N})$ , a substance separating in rhombic crystals and decomposing at  $326^\circ$ . When left in contact with pyridine, the diketone slowly becomes transformed into diethyl 3-methylcyclohexan-3-ol-1-one-4:6-dicarboxylate, and the rate at which this change proceeds is indicated by treating separate portions of the product at successive intervals of time with hydrazine hydrate. The yield of bispyrazolone steadily diminishes.

Diethyl ethylidenebisacetoacetate is obtained as a viscid oil by mixing together ethyl acetoacetate, acetaldehyde, and a small amount of piperidine at  $-15^\circ$  to  $+5^\circ$ ; the aliphatic nature of the product is demonstrated by the formation of 4-ethylidenebis-3-methyl-5-pyrazolone, which crystallises in prismatic needles and decomposes at  $250^\circ$  (compare Rosengarten, Abstr., 1894, i, 547). The transformation product, diethyl 3:5-dimethylcyclohexan-3-ol-1-one-4:6-dicarboxylate, melting at  $79-80^\circ$ , and described by Knoevenagel as the unaltered diethyl ethylidenebisacetoacetate (Abstr., 1895, i, 50), when treated with hydrazine hydrate, yields a monopyrazolone derivative,



which crystallises in needles, decomposes at  $256^\circ$ , and dissolves either in acid or alkaline solutions.

The cyclic ketone reacts in its enolic form when treated in ethereal solution with sodium, benzoyl chloride, and pyridine, giving rise to the dibenzoyl derivative,  $\text{OBz} \cdot \dot{\text{C}} \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{OBz}$ , a pale yellow oil boiling at  $175-185^\circ$  under the atmospheric pressure and partly solidifying at the ordinary temperature. The phenylcarbamide,



of the cyclic ketone, produced by allowing its generators to interact for 5 months at the ordinary temperature, is a crystalline substance melting at  $210^\circ$ .

The three isomeric  $\beta_1$ -,  $\beta_2$ -, and  $\beta_3$ -esters, obtained by condensing ethyl acetoacetate with benzaldehyde in the presence of pyridine, are now regarded as stereoisomeric diethyl 3-methyl-5-phenylcyclohexan-3-ol-1-one-4:6-dicarboxylates. The phenylhydrazone of the  $\beta_1$ -modification crystallises from alcohol in needles decomposing at  $168-171^\circ$ . The  $\beta_1$ - and  $\beta_2$ -esters both yield the same pyrazolone,  $\text{C}_{17}\text{H}_{20}\text{O}_4\text{N}_2$ , melt-



ing at 257°, which is identical with that obtained from the isomeric  $\alpha_1$ -ester (compare Rabe, Abstr., 1901, i, 34). The  $\beta_3$ -ester gives rise to an isomeric *pyrazolone* crystallising in white needles and melting at 140°.

Diethyl 3-methyl-5-*m*-nitrophenylcyclohexan-3-ol-1-one-4 : 6-dicarboxylate, described by Knoevenagel and Schürenberg as diethyl *m*-nitrobenzylidenebisacetoacetate (Abstr., 1899, i, 214), when heated with an alcoholic solution of hydrazine hydrate, yields a *pyrazolone*,  $C_{17}H_{19}O_6N_3$ , crystallising in prisms melting at 260°; this forms an insoluble sulphate and a sodium derivative.

*p*-Nitrobenzaldehyde and ethyl acetoacetate give rise to two stereoisomeric cyclohexanone derivatives; the  $\beta_1$ -ester, first isolated by Knoevenagel (*loc. cit.*), melts at 164° and yields a *pyrazolone* separating from alcohol in rhombic crystals and melting at 280°; the  $\beta_2$ -ester, melting at 152°, furnishes a *pyrazolone* crystallising in lustrous leaflets decomposing at 260°.

The ethereal alkylidenebisbenzoylacetates, unlike the corresponding condensation products from ethyl acetoacetate, are not affected by piperidine. Diethyl methylenebisbenzoylacetate (m. p. 86°), when treated with hydrazine hydrate, furnishes a theoretical yield of 4-methylenebis-3-phenyl-5-pyrazolone, which crystallises from alcohol in leaflets, decomposes at 280°, and dissolves in dilute acid or solutions of the alkali hydroxides.

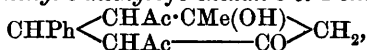
4-Benzylidenebis-3-phenyl-5-pyrazolone,  $C_{25}H_{20}O_2N_4$ , is a very soluble pyrazolone obtained by condensing diethyl benzylidenebisbenzoylacetate with hydrazine hydrate; 4-benzylidenebis-1-*p*-bromophenyl-3-phenyl-5-pyrazolone,  $C_{37}H_{26}O_2N_4Br_2$ , is produced from the same  $\delta$ -diketone by the action of *p*-bromophenyldiazine; it melts and decomposes at 290°.

The authors have obtained methylenebisacetylacetone only in the form of a viscid oil from which, after some months, a small quantity of a crystalline substance separates melting at 181° (compare Scholtz, Abstr., 1898, i, 43, and Knoevenagel, *ibid.*, i, 449).

4-Methylenebis-3 : 5-dimethylpyrazole,  $CH_2(C \begin{smallmatrix} \swarrow CMe \cdot NH \\ \nwarrow CMe \cdot N \end{smallmatrix})_2$ , prepared

by the action of hydrazine hydrate on the preceding  $\delta$ -diketone, crystallises in rhombohedra and melts at 280°; it readily dissolves in alcohol, but is only sparingly soluble in water. The  $\delta$ -diketone undergoes transformation under the influence of piperidine, but neither the cyclohexanone nor its pyrazole could be obtained in a state of purity.

4 : 6-Diacetyl-5-phenyl-3-methylcyclohexan-3-ol-1-one,



obtained by Knoevenagel, and also by Schiff (Abstr., 1895, i, 50, and 1900, i, 39), by condensing acetylacetone with benzaldehyde, is shown to be a cyclic compound by yielding a *pyrazole*,  $C_{17}H_{28}O_2N_2$ , with hydrazine hydrate; this compound crystallised in prisms and decomposed at 220°; the product of this reaction is at first contaminated with an azine, which is destroyed by boiling with dilute hydrochloric acid,  
G. T. M.

[ $\alpha$ -Glucoheptose.] By JULIUS WOHLGEMUTH (*Zeit. physiol. Chem.*, 1902, 35, 568—579).—The following compounds of  $\alpha$ -glucoheptose are described: the *phenylmethylhydrazone* forms white crystals melting at  $150^\circ$  and the *diphenylhydrazone* white crystals melting at  $140^\circ$ ; the osazone in pyridine alcohol mixture has the rotation  $+0^\circ 30'$ .  $\alpha$ -Glucoheptose does not give the resorcinol reaction, but with orcinol and phloroglucinol its reactions are very like those of the pentoses; these two reactions are believed to be characteristic of sugars with an uneven number of carbon atoms.

W. D. H.

The Influence of Pressure on the Inversion of Cane Sugar by Sucrase. By VICTOR HENRI (*Compt. rend. Soc. Biol.*, 1902, 54, 352—353).—Increase of pressure up to 400—800 atmospheres very slightly accelerates the inversion of cane sugar by sucrase. According to Röntgen, increase of pressure has the opposite effect on inversion by acids.

W. D. H.

Influence of the Concentration of Cane Sugar on the Rapidity of Inversion by Sucrase. By VICTOR HENRI (*Compt. rend. Soc. Biol.*, 1902, 54, 610—611).—No proportionality was observed between the concentration of solution of cane sugar and the rapidity of its inversion by sucrase, as described by Brown (*Trans.*, 1902, 81, 373).

W. D. H.

Action of Sodium Chloride on Inversion by Sucrase. By VICTOR HENRI (*Compt. rend. Soc. Biol.*, 1902, 54, 611—612).—Sodium chloride is taken as an example of a neutral salt; a constant quantity of salt inhibits inversion to a greater extent when a strong solution of cane sugar is employed than when a weak one is used. Its inhibiting action is greater when the amount of sucrase present is small.

W. D. H.

Action of Neutral Salts on the Inversion of Cane Sugar by Sucrase. By VICTOR HENRI (*Compt. rend. Soc. Biol.*, 1902, 54, 353—354).—The results show that various neutral salts exercise an inhibiting power on the rate of inversion of cane sugar by sucrase, and that there is a parallelism between this action and their capacity of precipitating colloids.

W. D. H.

Velocity of Hydrolysis of Acetylated Monoses and Bioses. By ROBERT KREMAN (Monatsh., 1902, 23, 479—488. Compare this vol., i, 134).—The rate of hydrolysis,  $k$ , is determined for the penta-acetyldextrose and -galactose, tetra-acetyl-galactose, tetra-acetylchloro-dextrose, and -chlorogalactose, and octo-acetyl-lactose, -maltose, and -sucrose with sodium hydroxide in 96 per cent. alcohol. The value of  $k$  for tetra-acetyl-galactose remains almost constant throughout the hydrolysis, but for the other acetyl compounds  $k$  diminishes gradually, in some cases to half of its original value. This is due to a difference in the rate of hydrolysis of the different acetyl groups, the most reactive acetyl group of penta-acetyl-galactose being absent in the tetra-acetyl derivative. As the value of  $k$  is smaller for the acetyl-

dextroses than for the acetylgalactoses, the acetyl groups in the former are less reactive, this observation is made use of to explain the formation of tetra-acetylnitrodextrose, and the non-formation of tetra-acetylnitrogalactose, from the corresponding chloro-compounds. The value of  $k$  for octo-acetyl-lactose, which contains a dextrose and a galactose grouping, is greater than that for octo-acetylmaltose, which contains two dextrose groupings. The rate of hydrolysis of octo-acetylsucrose lies between that of octo-acetyl-lactose and that of octo-acetylmaltose, approximating more nearly to the former. Tetra-acetylchlorogalactose is obtained in large, rhombic crystals. Attempts to prepare tetra-acetyldextrose by the action of silver carbonate and metallic sodium on tetra-acetylchlorodextrose resulted apparently in the complete decomposition of the acetyl derivative.

G. Y.

**Preparation and Properties of Crystallised Gentiobiose.** By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1902, 135, 290—292. Compare Abstr., 1901, i, 258).—Gentiobiose has now been obtained in a crystalline form by extracting the crude mixture of sugars produced by the partial hydrolysis of gentianose first with ethyl alcohol to remove lævulose and then with methyl alcohol to dissolve out the new hexobiose. The product crystallising from the latter solvent is white, hygroscopic, and has a bitter taste; it consists of gentiobiose combined with 2 mols. of methyl alcohol and has the formula  $C_{12}H_{22}O_{11} \cdot 2MeOH$ . These crystals melt at  $85.5-86^\circ$  (corr.), become solid on further heating, and fuse again at  $189-195^\circ$  to a yellow liquid; the alcohol of crystallisation is removed only by heating at  $100-115^\circ$ . When in solution, the substance exhibits the phenomenon of multirotation, the optical activity of the dextrorotatory solution diminishing to a minimum after 19 hours, the specific rotation at this stage being  $+8.33^\circ$ .

Gentiobiose separates from ethyl alcohol in crystals having the composition  $C_{12}H_{22}O_{11}$ . In this form it also exhibits multirotation, but the optical activity of its solution increases until a maximum is reached after 6 hours, giving  $[\alpha]_D 9.61^\circ$ .

This value of the specific rotation corresponds with that obtained for the crystals separating from methyl alcohol, providing that allowance is made for the solvent contained in this preparation.

G. T. M.

**Action of Enzymes on Hemicelluloses.** By J. GRÜSS (*Chem. Centr.*, 1902, i, 1277; from *Woch. Brauerei*, 19, 243—245).—Galactose is formed by the action of diastase powder prepared by Lintner's method on tragacanth, and under similar conditions mannan, the hemicellulose obtained from the endosperm of date seeds, yields mannose. By the action of the enzyme contained in the date itself, mannan is converted into mannose about twice as quickly as by a 5 per cent. solution of Lintner's diastase. Hence the hemicelluloses contained in barley are attacked by diastase, and by its prolonged action the same sugars are formed as those obtained by the action of acids.

The original paper also contains a description of experiments in which similar results were obtained by using two diastases prepared from barley malt and oat malt by Heinzelmann's methods.

E. W. W.

**Organic Vapour in the Air.** By H. HENRIET (*Compt. rend.*, 1902, 135, 101—103).—Air contains an organic vapour which seems to be a substituted formamide,  $\text{NHR}\cdot\text{CHO}$ . It is slowly converted into carbon dioxide by the action of the oxygen of the air, and if the air is moist and the moisture is condensed, the resulting water reduces silver nitrate solution on boiling, converts mercuric chloride into mercurous chloride, and reduces gold chloride and alkaline potassium permanganate. With Nessler's reagent, it gives a yellowish-green opalescence, especially if the liquid is previously heated with a small quantity of potassium hydroxide or of hydrochloric acid. The reducing power disappears if the condensed moisture is evaporated with sulphuric acid; if it is evaporated with hydrochloric acid, the residue gives the isonitrile reaction for primary amines.

C. H. B.

**Dialkylamides of isoValeric and  $\alpha$ -Bromoisovaleric Acids.** ARTHUR LIEBRECHT (D.R.-P. 129967).—isoValerodimethylamide, prepared by the action of isovaleryl chloride on dimethylamine dissolved in ether, boils at 188—192° under the ordinary pressure; the corresponding diethylamide and the diisoamylamide boil at 210—212° and 270—275° respectively under the ordinary pressure; the latter derivative is produced by heating diisoamylamine with isovaleric anhydride, isovaleroamide, or ethyl isovalerate under pressure.

$\alpha$ -Bromoisovalerodiethylamide results from the interaction of diethylamine and  $\alpha$ -bromoisovaleryl bromide in ethereal solution; it boils at 130—135° under 20 mm. pressure.

G. T. M.

**Hydroxyisopropylphosphinic Acid.** By CH. MARIE (*Compt. rend.*, 1902, 135, 106—108).—The methyl ester of hydroxyisopropylphosphinic acid (this vol., i, 431) melting at 76° and the ethyl ester which is liquid at the ordinary temperature are readily prepared by the action of the corresponding iodides on the silver salt. They decompose when distilled, yielding acetone and products which are still under investigation. When the esters are treated with an alkali hydroxide, decomposition takes place in two well marked stages, the first change being practically instantaneous, whilst the other necessitates the addition of a large excess of alkali and the prolonged boiling of the liquid. When treated with benzoyl chloride in presence of excess of pyridine, the acid yields benzoylisopropylphosphinic acid,  $\text{OBz}\cdot\text{C}_3\text{H}_6\cdot\text{PO}_3\text{H}_2$ , a crystallisable compound which melts at 102° and forms a white, crystallisable silver salt,  $\text{OBz}\cdot\text{C}_3\text{H}_6\cdot\text{PO}_3\text{Ag}_2$ . The above facts show that the constitution of the acid is  $\text{OH}\cdot\text{CMe}_2\cdot\text{PO}(\text{OH})_2$ .

C. H. B.

**Separation of Cyclic Aromatic Oxides or Sulphides from Coal Tar Hydrocarbons.** AKTIEN-GESELLSCHAFT FÜR THEER- & ERDÖL-INDUSTRIE (D.R.-P. 130679).—Mixtures of hydrocarbons containing

cyclic oxides or sulphides are fused with potassium hydroxide, the fused product being subsequently lixiviated with water. Under these conditions, the oxides become converted into the soluble potassium derivatives of the diphenols,  $O(C_6H_4)_2 + 2KOH = C_{12}H_8(OK)_2 + H_2O$ , and are thus separated from the insoluble hydrocarbons. G. T. M.

**Derivatives of 1:3-Dichloro-4:6-dinitrobenzene.** By JAN JOHANNES BLANKSMA and P. C. E. MEERUM TERWOGT (*Rec. trav. chim.*, 1902, 21, 286—291).—The authors have studied the nitration products of *m*-dichlorobenzene. By the action of sodium ethoxide on 1:3-dichloro-4:6-dinitrobenzene, 1:3-diethoxy-4:6-dinitrobenzene (diethyl-4:6-dinitroresorcinol) is obtained melting at 133°. 1:3-Dimethoxy-4:6-dinitrobenzene is formed in a similar manner; it melts at 157°, even after repeated crystallisation from methyl alcohol, the melting point given by Loring Jackson and Warren (*Abstr.*, 1891, 1024) being 167°. On heating this compound with alcoholic ammonia, the corresponding 4:6-dinitro-*m*-phenylenediamine is obtained, and on heating it with hydrochloric acid in a sealed tube, 4:6-dinitroresorcinol is formed. When 1:3-dichloro-4:6-dinitrobenzene is heated with methylamine in alcoholic solution, the chlorine atoms are replaced and there is produced 4:6-dinitro-1:3-dimethyl-*m*-phenylenediamine, which forms small, yellow crystals, sparingly soluble in alcohol or acetic acid, and does not melt even at 280°. On dissolving the latter in nitric acid and heating the solution for a short time, 2:4:6-trinitro-*m*-phenylene-1:3-dimethyldinitroamine,  $C_6H(NMe \cdot NO_2)_2(NO_3)_3$ , is formed.

A. F.

**Preparation of Aromatic Sulphinic Acids.** BASLER CHEMISCHE FABRIK (D.R.-P. 130119).—The aromatic sulphinic acid is obtained by adding to the cold diazo-solution a 40 per cent. solution of sodium hydrogen sulphite and excess of alcoholic sulphurous acid containing a small quantity of cupric sulphate or other compound of copper. The reaction occurs at 0—20° in the case of aniline, *o*-toluidine, or methyl anthranilate, but more stable diazo-salts require a higher temperature. The solution obtained from *o*-anisidine must be warmed to 30°.

G. T. M.

**Nitrodihydrophenanthrene.** JULIUS SCHMIDT (D.R.-P. 129990. Compare *Abstr.*, 1901, i, 76).—Finely divided phenanthrene, when mixed with the liquefied crude product of the action of nitric acid on starch or arsenious oxide, takes up the elements of nitrous acid and yields *nitrodihydrophenanthrene*,  $C_{14}H_{11}O_2N$ ; this substance is a yellow, crystalline powder, softening at 70° and decomposing at 100°; it readily dissolves in the ordinary organic solvents.

G. T. M.

**Reduction of Aromatic Nitro-compounds to Amines.** C. F. BOEHRINGER & SÖHNE (D.R.-P. 130742).—Nitrobenzene, when gradually added to copper powder suspended in concentrated sodium chloride solution contained in the cathode compartment of an electrolytic cell, is quantitatively reduced to aniline at 80—100° by a current of 1500 amperes per square metre and 5 volts. A copper cathode is employed, whilst the anode compartment contains a carbon anode surrounded by concentrated sodium chloride solution.

Under similar conditions, *o*-nitrotoluene and  $\alpha$ -nitronaphthalene readily yield *o*-toluidine and  $\alpha$ -naphthylamine, whilst *m*-nitroaniline is reduced to *m*-phenylenediamine, the yield being 80 per cent.

G. T. M.

**Action of Formaldehyde [on Ethylaniline].** By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1902, 26, 606. Compare Abstr., 1900, i, 436).—A mixture of monoethylaniline, formaldehyde, and hydrochloric acid forms, after some days, the compound  $\text{NEtPh}\cdot\text{CH}_2\text{Cl}$ . This melts at  $250^\circ$  and is soluble in hot water; alkali hydroxides added to its dilute aqueous solution separate a base which is soluble in chloroform and may be obtained pure by precipitating the solution with ether.

Similar compounds may be obtained in this manner from the esters of the three aminobenzoic acids, and mention is made of the production of compounds by the action of formaldehyde on benzoylthymol, phenylhydrazine, and acetylphenylhydrazine.

By treating resacetophenone for 2 hours with formaldehyde and hydrochloric acid and boiling the product with xylene, an insoluble compound is obtained which, however, dissolves in chloroform and is precipitated from the solution by addition of ether. The xylene contains a second product which separates as a white, crystalline substance melting at  $245\text{--}250^\circ$  and is soluble in the alkali hydroxides.

L. DE K.

**Iodo-derivatives of Aromatic Aminosulphonic Acids.** KALLE & Co. (D.R.-P. 129808).—The aromatic amines, when treated with iodine monochloride, give rise to tarry products; their monosulphonic acids, on the other hand, furnish well-defined iodo-derivatives when treated with hydrochloric acid solutions of this reagent.

*Iodosulphanilic acid* crystallises from its concentrated aqueous solutions in small, white needles. *Di-iodosulphanilic acid*, resulting from the action of excess of iodine monochloride on sulphanilic acid, separates from dilute aqueous solutions on the addition of sodium chloride. *Di-iodometanilic acid* crystallises from water in colourless leaflets. The diazo-compounds of these iodoaminosulphonic acids are yellow.

G. T. M.

**Trisubstituted Naphthalene Derivatives.** By ARTURO JACCHIA (*Annalen*, 1902, 323, 113—134).—6-Nitro- $\beta$ -naphthylamine-8-sulphonic acid is most conveniently obtained by nitrating  $\beta$ -naphthylamine-8-sulphonic acid dissolved in concentrated sulphuric acid with potassium nitrate. The 2:6-diaminonaphthalene-8-sulphonic acid produced by reducing the nitro-compound yields 2:6-diaminonaphthalene on treatment with sodium amalgam and was formerly supposed to be identical with the compound prepared by heating 2:6-dihydroxynaphthalenesulphonic acid with ammonia under pressure (D.R.-P. 72222). An examination of the latter diamino-acid showed that the commercial product consists of a mixture of free sulphonic acids and their sodium salts, the principal constituent of which is a diaminonaphthalenedisulphonic acid. This substance, which is insoluble in alcohol, crystallises from water in leaflets having a silvery

lustre and the composition  $C_{10}H_4(NH_2)_2(SO_3H)_2 \cdot 4\frac{1}{2}H_2O$ ; when the aqueous solution is treated with sodium amalgam, 2:6-diamino-naphthalene is produced.

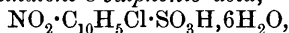
The *ammonium* salt of 6-nitro- $\beta$ -naphthylamine-8-sulphonic acid crystallises in dark red, anhydrous prisms; the *barium* salt separates in red crystals with  $4\frac{1}{2}H_2O$ .

The *anhydride* of 6-nitro-2-diazonaphthalene-8-sulphonic acid, obtained by diazotising the preceding ammonium salt, is very sparingly soluble in cold water; it combines with aniline, yielding a red colouring matter, and when boiled with water gives rise to 6-nitro- $\beta$ -naphthol-8-sulphonic acid,  $NO_2 \cdot C_{10}H_5(OH) \cdot SO_3H \cdot 4H_2O$ , which crystallises from water in light yellow prisms and retains  $2H_2O$  even at  $150^\circ$ ; the *potassium* salt,  $NO_2 \cdot C_{10}H_5(OH) \cdot SO_3K$ , separates in anhydrous, orange prisms; the *barium* salt,  $[NO_2 \cdot C_{10}H_5(OH) \cdot SO_3]_2Ba \cdot 6\frac{1}{2}H_2O$ , crystallises in dark yellow prisms; the *sodium* salt is less definite and crystallises either with 5 or  $6H_2O$ .

6-Amino- $\beta$ -naphthol-8-sulphonic acid,  $NH_2 \cdot C_{10}H_5(OH) \cdot SO_3H \cdot H_2O$ , produced by reducing the nitro-compound with stannous chloride, crystallises from water in lustrous, grey needles; it is somewhat unstable, and when boiled with an emulsion of barium carbonate yields the barium salt of a dark blue colouring matter, the composition of which approximates to that required by the formula  $(C_{40}H_{24}O_{16}N_4S_4)Ba_2$  or  $(C_{40}H_{28}O_{16}N_4S_4)Ba_2$ .

6-Amino- $\beta$ -naphthol results from the action of sodium amalgam on the preceding sulphonic acid dissolved in an aqueous solution of sulphur dioxide; it crystallises from water in grey flakes which decompose at  $190$ – $195^\circ$  and rapidly assume a blue colour on exposure to the air.

2-Chloro-6-nitronaphthalene-8-sulphonic acid,



obtained from 6-nitro-2-diazonaphthalene-8-sulphonic acid by the Sandmeyer reaction, crystallises from water in bright yellow, silky prisms; the *barium* salt crystallises in deep yellow needles with  $7H_2O$ ; the *silver* salt separates in anhydrous, yellowish-brown needles.

6-Chloro- $\beta$ -naphthylamine-8-sulphonic acid,  $NH_2 \cdot C_{10}H_5Cl \cdot SO_3H$ , produced by reducing the preceding nitro-compound, is precipitated from the aqueous solution of its sodium salt by excess of hydrochloric acid and crystallises in brown, silky prisms with a violet reflex; the *barium* salt forms very soluble, light brown leaflets. G. T. M.

*m*-Chloro- and *m*-Bromo-trinitrophenols. By S. TIJMSTRA (*Rec. trav. chim.*, 1902, 21, 292–293).—On nitrating *m*-chlorophenol with a mixture of nitric and sulphuric acids, 3-chloro-2:4:6-trinitrophenol is obtained in yellow crystals melting at  $119^\circ$ . In the same manner, *m*-bromophenol gives 3-bromo-2:4:6-trinitrophenol, which melts at  $144^\circ$ . On treating these compounds with sodium methoxide, the halogen is replaced by the methoxy-group. A. F.

**Ionic Phenomena Exhibited by Triphenylmethane Colouring Matters.** By OTTO FISCHER (*Chem. Centr.*, 1902, ii, 91; from *Zeit. Farben-Textil-Chem.*, 1902, i, 281).—If an excess of concentrated hydro-

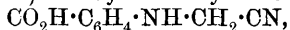
chloric acid is added to a solution containing a trace of rosaniline, methyl-violet, or malachite-green dissolved in dilute hydrochloric acid, until the liquid becomes yellow, a point may be reached at which the solution no longer shows the slightest coloration when poured into water, but, on the other hand, when added to alcohol, the red, violet, or green ions of the respective dyes are at once apparent. The same phenomena are shown by solutions of the colouring matters in concentrated sulphuric acid (compare also Kehrman and Wentzel, this vol., i, 89). E. W. W.

**7-Amino- $\beta$ -naphtholsulphonic Acid.** LEOPOLD CASSELLA & Co. (D.R.-P. 131526).—7-Amino- $\beta$ -naphthol readily yields a disulphonic acid, even on treatment with 90 per cent. sulphuric acid; this product readily parts with one of the sulphonic groups on hydrolysis with dilute acids and yields 7-amino- $\beta$ -naphtholsulphonic acid. The sodium salt,  $\text{OH}\cdot\text{C}_{10}\text{H}_5(\text{NH}_2)\cdot\text{SO}_3\text{Na}\cdot\text{H}_2\text{O}$ , separates in sparingly soluble nodular aggregates; the *dial*zo-compound is yellow and sparingly soluble in water. G. T. M.

**Preparation of Anthranilic Acid from 4-Sulphoanthranilic Acid.** KALLE & Co. (D.R.-P. 129165).—When treated in aqueous solution with sodium amalgam, 4-sulphoanthranilic acid, obtained by the action of sodium hydroxide solution on *o*-nitrotoluene-4-sulphonic acid, readily loses its sulphonic group and gives rise to anthranilic acid. G. T. M.

**Preparation of Anthranilic Acid.** BASLER CHEMISCHE FABRIK (D.R.-P. 130301, 130302).—Phthalylhydroxylamine (this vol., i, p. 720) or its alkali derivatives, when heated with sodium or potassium carbonate in aqueous or alcoholic solution, becomes converted into the corresponding alkali anthranilate. G. T. M.

**$\omega$ -Cyanomethylanthranilic Esters.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 129562).— $\omega$ -Cyanomethylanthranilic acid,



readily yields its *ethyl* ester when treated at  $100^\circ$  with ethyl bromide in the presence of sodium hydroxide solution or milk of lime; this derivative melts at  $89^\circ$ , whilst the *methyl* ester, prepared by means of methyl sulphate or the methyl ester of an aromatic sulphonic acid, melts at  $108^\circ$ . The methylation with methyl sulphate takes place at  $50^\circ$ . G. T. M.

**Action of Sulphites on Aromatic *o*-Hydroxycarboxylic Acids.** By HANS BUCHERER (*Zeit. Farben- Textil-Chem.*, 1902, 1, 477—480. Compare Abstr., 1901, i, 695, and this vol., i, 91).—Although 2-hydroxy-3-naphthoic acid is converted into 2-amino-3-naphthoic acid by the action of ammonia solution at  $260^\circ$  (Möhlau, Abstr., 1894, i, 138), yet, when heated with a mixture of this reagent and ammonium sulphite at  $125^\circ$ , it loses its carboxyl group and becomes converted into  $\beta$ -naphthylamine. The acid also loses its carboxyl group when heated with a solution containing both sodium



hydrogen sulphite and sodium hydroxide; in this case,  $\beta$ -naphthol is produced.

1-Hydroxy-2-naphthoic acid and 2-hydroxy-1-naphthoic acid both very readily lose their carboxyl radicles under these conditions, yielding a naphthylamine in the presence of ammonia and a naphthol under the influence of an alkali hydroxide.

Salicylic acid, on the other hand, is very stable towards hot solutions of the sulphites, and remains unaffected when treated in the manner indicated. G. T. M.

**Derivatives of the Nitrophthalic Acids.** By HEINRICH SEIDEL and J. C. BITTNER (*Monatsh.*, 1902, 23, 415—436. Compare Miller, *Annalen*, 1881, 208, 294).—3-Nitrophthalimide, formed when 3-nitrophthalic acid is heated at 220° in a stream of dry ammonia gas, crystallises in yellowish-white needles, melts at 216°, sublimes unchanged, and is easily soluble in alcohol, glacial acetic acid, acetone, or solutions of the alkali hydroxides; it dissolves with difficulty in hot water but is insoluble in the cold solvent; the imide is converted, by Hofmann's reaction, into 6-nitroanthranilic acid, melting at 184°, an isomeride of Hübner's 3-nitroanthranilic acid (*Abstr.*, 1879, 380); it has a sweet taste, is easily soluble, and yields a deep orange-red, crystalline, sodium salt and a hydrochloride crystallising in long, almost colourless, needles. When heated with alcohol and hydrochloric acid, 6-nitroanthranilic acid yields a small amount of *m*-nitroaniline but no ester; when heated with diluted sulphuric acid (1:1) at 120°, it is converted into *m*-nitroaniline, and when diazotised and boiled with dilute sulphuric acid it yields *m*-nitrophenol. Reduction by tin and hydrochloric acid leads to the formation of 2:6-diaminobenzoic acid, the hydrochloride of which forms colourless, glistening needles; these become greyish-violet on exposure to light and air, and are easily soluble in alcohol but not in ether. Reduction in presence of excess of hydrochloric acid and rapid evaporation of the liquid leads to the formation of *m*-phenylenediamine.

4-Nitrophthalimide, formed at 170° from 4-nitrophthalic acid, crystallises in yellow, glistening leaflets, melts at 202°, sublimes unchanged, has solubilities similar to those of the 6-isomeride, and yields the two possible isomeric nitroanthranilic acids.

5-Nitroanthranilic acid crystallises from dilute alcohol in lemon-yellow, silky needles, melts at 280°, and not at 263° as stated by Hübner (*loc. cit.*), is insoluble in xylene, yields an ethyl ester which melts at 146° (Kaiser, *Abstr.*, 1886, 149) and an acetyl derivative melting at 214—216°; it is converted by diazotisation into 5-nitrosalicylic acid melting at 288° (Hübner, *Abstr.*, 1882, 503; Rupe, *Abstr.*, 1897, i, 416), and reduced by tin and hydrochloric acid to a colourless solution which gives the *p*-phenylenediamine reactions either with aniline hydrochloride and potassium dichromate or with ferric chloride.

4-Nitroanthranilic acid [ $\text{NH}_2 : \text{CO}_2\text{H} : \text{NO}_2 = 2 : 1 : 4$ ] separates from dilute alcohol as a yellow, crystalline powder having an intensely sweet taste; it is soluble in xylene and forms an orange-red, crystalline sodium salt, easily soluble in water, and a hydrochloride which crystallises in long, delicate, glistening leaflets and dissociates on drying.

The *ethyl ester*, formed by the action of alcohol and hydrogen chloride, separates from dilute alcohol in clusters of yellow needles melting at  $91^{\circ}$  and when crystallised from benzene melts at  $89^{\circ}$ ; it has a burning, sweet taste, is insoluble in aqueous sodium carbonate solution, and soluble in benzene. The *acetyl* derivative crystallises in long, slightly yellow needles and melts at  $188^{\circ}$ . Diazotisation of the 4-acid leads to the formation of 4-*nitrosalicylic acid*, which crystallises in broad, short, orange-yellow needles, melts at  $235^{\circ}$ , has a bitter taste, is easily soluble in alcohol, chloroform, or benzene, but insoluble in light petroleum, and gives a blood red coloration with ferric chloride. This nitro-compound is reduced by tin and hydrochloric acid to 4-*aminosalicylic acid*, which forms a reddish-brown, crystalline powder, melts at  $220^{\circ}$ , is easily soluble in water or alcohol, but more sparingly so in ether, forms a *hydrochloride* which is easily oxidised to a dark brown mass on exposure to air, gives an intense dark violet coloration with ferric chloride, and on diazotisation and boiling yields a solution which gives the reactions of 2:4-dihydroxybenzoic acid.

Reduction of 4-nitroanthranilic acid by tin and hydrochloric acid leads to the formation of 2:4-*diaminobenzoic acid*, which is easily decomposed into carbon dioxide and *m*-phenylenediamine.

G. Y.

**Phthalylhydroxylamine.** BASLER CHEMISCHE FABRIK (D.R.-P. 130680, 130681).—Phthalylhydroxylamine is produced by the interaction of hydroxylamine hydrochloride and sodium carbonate in aqueous solution on phthalic anhydride, the reagents being present in molecular proportion. When excess of sodium carbonate is added, the intermediate product, *phthalhydroxylamic acid*,  $\text{OH}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , may be isolated, being precipitated from the alkaline solution by hydrochloric acid; this substance melts at  $204\text{--}206^{\circ}$  and is readily soluble in alcohol or water; its aqueous solution, when warmed at  $50^{\circ}$ , yields phthalylhydroxylamine. G. T. M.

**Monoacyl Derivatives of Indoxyl and Indoxylic Acid.** DANIEL VORLÄNDER & BRUNO DRESCHER (D.R.-P. 131400).—In addition to the results already published (compare Abstr., 1901, i, 563), the following compounds are described for the first time.

3-*Propionylindoxyl*, obtained by treating the decomposition product of phenylglycinecarboxylic acid with propionic acid and propionic anhydride, is insoluble in solutions of the alkali hydroxides and melts at  $87^{\circ}$ . An isomeride, 1-*propionylindoxyl*, produced by treating indoxyl with propionic anhydride suspended in water, melts at  $128^{\circ}$  and is soluble in alkalis.

1-*Benzoylindoxyl*, prepared from indoxyl by the Schotten-Baumann reaction, crystallises from dilute acetic acid and melts at  $101^{\circ}$ ; its *nitroso*-derivative crystallises in pale yellow needles and melts at  $104^{\circ}$ .

3-*Benzoylindoxyl*, resulting from the action of benzoic anhydride on indoxyl at  $40^{\circ}$ , crystallises from alcohol, melts at  $123^{\circ}$ , and is soluble in a solution of an alkali hydroxide; its isomeride does not dissolve in this medium.

*Sodium acetylindoxylate*, formed by the action of acetic anhydride on a slightly alkaline solution of sodium indoxylate, crystallises in lustrous

white leaflets containing water of crystallisation. The corresponding salts of calcium and the heavy metals are sparingly soluble in water; the magnesium salt separates in glistening leaflets. G. T. M.

**Action of Solid Alkalis on Aromatic Aldehydes.** By P. N. RAIKOW and J. RASCHTANOW (*Chem. Centr.*, 1902, i, 1212—1213; from *Oesterr. Chem. Zeit.*, 5, 169—173).—By the action of solid alkali hydroxide on benzaldehyde, *p*-tolylaldehyde, cuminaldehyde, and *o*-chlorobenzaldehyde, theoretical quantities of alcohols and acids are formed. The reaction with benzaldehyde takes place without the formation of any resinous bye-products (compare Meyer, *Abstr.*, 1882, 195). When the chlorobenzaldehydes are similarly treated, the chlorine is divided equally between the two products. *o*-Chlorobenzyl alcohol crystallises in white, lustrous leaflets, melts at 69.5°, and is only very slightly soluble in water, but readily so in alcohol or ether. *p*-Chlorobenzaldehyde is only slowly attacked by alkali; *p*-chlorobenzyl alcohol melts at 71°. Salicylaldehyde, *p*-hydroxybenzaldehyde, and vanillin do not undergo Cannizzaro's reaction with the alkali hydroxides. Anisaldehyde forms anisic acid, which melts at 178.5°. The presence of a hydroxyl group in the ortho- or para-position renders the aldehyde incapable of reacting with alkalis. *o*-Nitrobenzaldehyde yields an acid which decomposes completely at 190—200°, and contains 7.5 per cent. of nitrogen. *p*-Nitrobenzaldehyde and its *m*-isomeride do not form alcohols, but by saturating the products with hydrogen chloride, amorphous substances containing 6 and 8.1 per cent. of nitrogen respectively are obtained. Thus the nitrobenzaldehydes do not yield the normal products, but either form acids with loss of a portion of the nitrogen or compounds in which hydroxyl groups are present in the benzene ring. E. W. W.

**$\alpha$ -Substituted Anthraquinone Derivatives containing Chlorine or Bromine.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 131538).— $\alpha$ -Diazoanthraquinone, when treated with hydrochloric or hydrobromic acid, yields the corresponding halogen derivative. In this reaction, the presence of cuprous salts is not essential. G. T. M.

**Blue Colouring Matter of the Anthracene Series.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 129845, 129846, 129847, 129848).—2-Aminoanthraquinone, when melted with potassium hydroxide at 200—300°, yields a leuco-compound which, by aerial oxidation, changes into a pigment closely resembling indigotin; it is insoluble in solutions of the mineral acids or the alkali hydroxides, and crystallises from nitrobenzene in blue needles with a copper-bronze lustre. This substance,  $C_{14}H_7O_2N$ , which may also be obtained from 2-aminohydroxyanthranol, yields a yellow product, and, on oxidation by alkaline reducing agents, is converted into the soluble leuco-derivative.

2-Aminoanthraquinonesulphonic acid, when submitted to fusion with potash at 170—175°, yields the sulphonic acid of the pigment  $C_{14}H_7O_2N$ , a soluble, blue colouring matter, which may also be obtained by sulphonating the insoluble compound with fuming sulphuric acid, either with or without boric acid.

The *sodium* derivative of the leuco-compound can be isolated in the form of copper-coloured needles by reducing the insoluble colouring matter with a solution of sodium hyposulphite and sodium hydroxide; it dissolves in warm, alkaline solutions, but is readily dissociated by water, regenerating the pigment. G. T. M.

**Anthracene Colouring Matters containing Nitrogen.** FAR-BENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 127439).—2-Bromo-4-nitro-1-hydroxyanthraquinone is obtained by heating 4-nitro-1-hydroxyanthraquinone-2-sulphonic acid with bromine at 120°; it crystallises from glacial acetic acid in lustrous, yellow needles, dissolving in concentrated sulphuric acid to a light yellow solution which becomes reddish-yellow on the addition of boric acid. When heated with primary aromatic amines, it yields blue colouring matters. By the action of *p*-toluidine, for example, the nitro-group is replaced by the tolylamino-radicle and a substance is obtained identical with that produced by condensing this amine with 2:4-dibromo-1-hydroxyanthraquinone. When boric acid is added during the fusion, the colouring matters are green. G. T. M.

**Preparation of Ionone.** HAARMANN & REIMER (D.R.-P. 129027).— $\psi$ -Ionone, when treated with warm dilute mineral acids, always yields  $\alpha$ -ionone mixed with varying quantities of its  $\beta$ -isomeride. The latter compound is formed almost exclusively when the transformation is induced by 70 to 100 per cent. sulphuric acid in the cold, whereas  $\alpha$ -ionone containing only traces of the isomeric compound is produced when the reaction is carried out with concentrated phosphoric acid at 30° (compare Abstr., 1901, i, 157; this vol., i, 342, 471).

G. T. M.

**New Syntheses in the Terpene Series.** By OTTO WALLACH (*Chem. Centr.*, 1902, i, 1293—1296; from *Nachr. k. Ges. Wiss. Göttingen*, 1902, 92—107). [With NICOLAI SPERANSKI.] (Compare Abstr., 1901,

i, 155).—*Ethyl cyclopentanolacetate*,  $\begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{matrix} > \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ ,

produced by the influence of zinc on *cyclopentanone* and *ethyl bromoacetate*, boils at 105—107° under 11 mm. pressure. By the elimination of water, it forms an unsaturated *ester*,  $\text{C}_9\text{H}_{14}\text{O}_2$ , which boils at 82—84° under 11 mm. pressure. The corresponding *acid*,  $\text{C}_7\text{H}_{10}\text{O}_2$ , melts at 49—50° and boils at 122° under 11 mm. pressure; the *dibromide*,  $\text{C}_7\text{H}_{10}\text{Br}_2\text{O}_2$ , melts at 88°, and the *amide*,  $\text{C}_6\text{H}_9 \cdot \text{CO} \cdot \text{NH}_2$ , at 144°. The unsaturated *ester*,  $\text{C}_{10}\text{H}_{16}\text{O}_2$ , derived from *ethyl  $\beta$ -methylcyclopentanolacetate*, boils at 90—92° under 11 mm. pressure; its *acid*,  $\text{C}_8\text{H}_{12}\text{O}_2$ , boils at 128° under 10 mm. pressure or about 240° under the ordinary pressure with liberation of carbon dioxide. The *nitrile*,  $\text{C}_7\text{H}_{11} \cdot \text{CN}$ , boils at 208—210°. The *amide*,  $\text{C}_7\text{H}_{11} \cdot \text{CO} \cdot \text{NH}_2$ , melting at 128°, together with a *hydrocarbon*,  $\text{C}_7\text{H}_{12}$ , is prepared by heating the ammonium salt of the unsaturated acid at 230°. The hydrocarbon boils at 96—97° and has a sp. gr. 0.7750 and  $n_D$  1.4336 at 16°.

Similarly, by means of the *ethyl bromoacetate* synthesis, from *dihydrocarvone* and *carvenone* on the one hand and *menthone* and *tetrahydrocarvone* on the other, unsaturated acids can be obtained

which decompose with liberation of carbon dioxide and formation of homoterpenes,  $C_{11}H_{18}$ , and homomenthenes,  $C_{11}H_{20}$ .

[With FRITZ THÖLKE.]—The *terpene*,  $C_{11}H_{18}$ , prepared from dihydrocarvone, boils at  $191-192^\circ$  and has a sp. gr. 0.8465 and  $n_D$  1.4771. The unsaturated *ester*,  $C_{10}H_{15}\cdot CH_2\cdot CO_2Et$ , from which it is derived, boils at  $145-148^\circ$  under 18 mm. pressure. The *terpene*,  $C_{11}H_{18}$ , obtained from carvenone, boils at  $194-197^\circ$  and has a sp. gr. 0.8510 and  $n_D$  1.4821. The unsaturated *ester*,  $C_{10}H_{15}\cdot CH_2\cdot CO_2Et$ , boils at  $135-137^\circ$  under 16 mm. pressure. *Menthene*,  $C_{11}H_{20}$ , prepared from menthone, boils at  $196-197^\circ$  and has a sp. gr. 0.8215 and  $n_D$  1.4579. The isomeric *menthene*,  $C_{11}H_{20}$ , from tetrahydrocarvone, boils at  $194-195^\circ$  and has a sp. gr. 0.8300 and  $n_D$  1.4619.

II. [With NICOLAI SPERANSKI.]—In order to distinguish between  $\alpha$ - and  $\beta$ -adipic acids, the methylpentanones obtained by distilling the calcium salts are condensed with benzaldehyde.  $\alpha$ -Methylpentanone yields a *monobenzylidene* derivative,  $C_5H_8O:C:CHPh$ , which crystallises in colourless needles and melts at  $123-124^\circ$ , whilst  $\beta$ -methylpentanone forms *dibenzylidene- $\beta$ -methylpentanone* melting at  $149-151^\circ$ . By means of this condensation, the acid obtained by oxidation of pulegone and methylhexanone has been proved to be  $\beta$ -methyladipic acid (compare Markownikoff, Abstr., 1900, i, 475). When  $\beta$ -methyladipic acid is distilled in a vacuum, it is partially converted into the anhydride; only a portion of the distillate is soluble in dry benzene and melts at  $84^\circ$ , whilst the insoluble residue melts at  $91^\circ$ .

III. [With O. RAHN.]—When the terpineol (m. p.  $32^\circ$ ) discovered by Helle and Stephan in liquid terpineol (compare Schimmel & Co., Abstr., 1901, i, 394) is treated with bromine and a solution of hydrogen bromide in glacial acetic acid, a *terpineol tribromide*,

$CMeBr\left<\begin{smallmatrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{smallmatrix}\right>CH\cdot CMeBr\cdot CH_2Br$ , is formed which melts at  $65^\circ$ .

By the oxidation of this compound with potassium permanganate, a *trihydroxy-derivative*,  $C_{10}H_{20}O_3$ , is obtained. This compound crystallises from ethyl acetate, melts at  $116-117^\circ$ , and when boiled with dilute sulphuric acid loses water and forms the compound  $C_{10}H_{16}O$ , which boils at  $217-225^\circ$  under atmospheric pressure, has a sp. gr. 0.977,  $n_D$  1.4930 at  $20^\circ$ , and is analogous to the isomeric compound prepared from the oxidation product,  $C_{10}H_{20}O_3$ , of dihydrocarveol. By warming the oxyketone,  $C_9H_{16}O_2$ , prepared by Helle and Stephan (*loc. cit.*), with dilute sulphuric acid or by oxidising the trihydroxy-terpineol with chromic acid, *tetrahydro- $p$ -tolyl methyl ketone*,

$CMe\left<\begin{smallmatrix} CH-CH_2 \\ CH_2\cdot CH_2 \end{smallmatrix}\right>CH\cdot COMe$ , is formed; it boils at  $205-206^\circ$ , has a sp. gr. 0.940, and  $n_D$  1.4719 at  $19^\circ$ , and when heated with sulphuric acid (4 vols.) yields *p*-tolyl methyl ketone. The *semicarbazone* of tetrahydro-*p*-tolyl methyl ketone melts at  $164-165^\circ$ . The *oxime* crystallises from dilute alcohol, melts at  $51-52^\circ$ , and is readily soluble in light petroleum. The *dibromo-oxime*,  $C_9H_{14}Br_2\cdot NOH$ , melts at  $130^\circ$ . The secondary *alcohol*,  $C_9H_{16}O$ , prepared by the action of sodium on an alcoholic or ethereal solution of the ketone, is a lower homologue of the terpineol melting at  $35^\circ$ ; it boils at  $212-213^\circ$ , has a sp. gr. 0.942, and  $n_D$  1.4836 at  $19^\circ$ .

When the oxylactone,  $C_{10}H_{16}O_3$ , prepared by oxidising pulegenic acid with potassium permanganate, is treated with a small quantity of concentrated sulphuric acid, the ketone *pulenone*,  $C_9H_{16}O$ , is formed which boils at  $183^\circ$  and has a sp. gr. 0.8925 and  $n_D$  1.44506 at  $21^\circ$ . *Pulenol*,  $C_9H_{18}O$ , obtained by reducing pulenone, boils at  $187$ — $189^\circ$ , has a sp. gr. 0.8953, and  $n_D$  1.4569 at  $20^\circ$ ; by the elimination of water it forms pulenene,  $C_9H_{16}$ . *Pulenene nitrosochloride*,  $C_9H_{16}\cdot NOCl$ , is a blue substance melting at  $88$ — $89^\circ$ . *Pulenoneoxime*,  $C_9H_{16}\cdot NOH$ , melts at  $94$ — $95^\circ$ ; *pulenoneisooxime* melts at  $96$ — $97^\circ$  and by the action of acids forms nonylenic acid. Both oximes are easily converted into the nitrile of nonylenic acid, which boils at  $216$ — $217^\circ$ .

[With COLMANN.]—*Pulegene*,  $C_9H_{16}$ , prepared by eliminating carbon dioxide from pulegenic acid, boils at  $138$ — $139^\circ$ , has a sp. gr. 0.791,  $n_D$  1.44, and on oxidation yields a ketonic acid,  $C_9H_{16}O_3$ , which boils at  $265^\circ$  or at  $164^\circ$  under 15 mm. pressure. The *semicarbazone* melts at  $164^\circ$  and *pulegene nitrosochloride*,  $C_9H_{16}\cdot NOCl$ , is a readily soluble, white substance.

[With THEDE.]—*Pulegene nitrolepiperidide*,  $C_9H_{16}ON\cdot C_5NH_{10}$ , melts at  $106$ — $107^\circ$ . By elimination of hydrogen chloride from the nitrosochloride, *pulegenoneoxime*,  $C_9H_{14}\cdot NOH$ , a liquid boiling at  $120$ — $125^\circ$  under 11 mm. pressure, is formed, and by the action of acids on this compound *pulegenone*,  $C_9H_{14}O$ , is obtained. The latter boils at  $189$ — $190^\circ$  and has a sp. gr. 0.914 and  $n_D$  1.4645. The *alcohol*,  $C_9H_{18}O$ , prepared by reducing pulegenone, boils at  $77$ — $78^\circ$  under 15 mm. pressure and on oxidation yields *dihydropulegenone*,  $C_9H_{16}O$ , which boils at  $188$ — $189^\circ$ , has a sp. gr. 0.889, and  $n_D$  1.4439 at  $20^\circ$  and is not attacked by cold potassium permanganate. The *semicarbazone* melts at  $176$ — $178^\circ$  and is very slightly soluble in alcohol. The *oxime* does not readily solidify.

[With A. SCHEUNERT.]—*cyclo-Geraniolene* resembles pulegene, boils at  $138$ — $139^\circ$ , and has a sp. gr. 0.8030 and  $n_D$  1.44406. The *nitrosochloride*,  $C_9H_{16}\cdot NOCl$ , and *nitrosate*,  $C_9H_{16}N_2O_4$ , have been prepared. The *nitrolepiperidide*,  $C_9H_{16}ON\cdot C_5NH_{10}$ , melts at  $136$ — $138^\circ$  and the *nitrobenzylamine*,  $C_9H_{16}ON\cdot NH\cdot C_7H_7$ , at  $106^\circ$ . By boiling with alcoholic potassium hydroxide, the nitrosochloride and nitrosate form *trimethylcyclohexenoneoxime*,  $C_9H_{14}\cdot NOH$ , which crystallises from ether or light petroleum, melts at  $128$ — $129^\circ$ , boils at  $131$ — $132^\circ$  under 15 mm. pressure, and by the action of acids forms *trimethylcyclohexenone*,  $C_9H_{14}O$ . The latter compound boils at  $195$ — $196^\circ$ , has a sp. gr. 0.9245, and  $n_D$  1.4749 at  $25^\circ$ , and appears to exist only in the enolic form. The *semicarbazone* melts at  $158$ — $159^\circ$  and is rather soluble in cold ether. By the action of sodium and alcohol on hexenone, a *pinacone* melting at  $128$ — $130^\circ$  and *trimethylcyclohexanol*,  $C_9H_{18}O$ , are formed. The latter is an oil, has the odour of camphor, boils at  $192$ — $193^\circ$ , and on oxidation yields *trimethylcyclohexanone*,  $C_9H_{16}O$ , which boils at  $191^\circ$  and has a sp. gr. 0.9 and  $n_D$  1.4548; the *oxime* melts at  $108$ — $109^\circ$ .

IV. [With KÖSCH.]—By the action of methyl iodide on the ethyl ester of aminodecic acid obtained from menthoneisooxime (Abstr., 1900, i, 589), a quaternary *iodide*,  $C_9H_{18}NMe_3I\cdot CO_2Et$ , melting at  $117^\circ$ , is formed, and by treating the chloride prepared from this compound

with silver oxide, an  $\epsilon$ -betaine,  $\text{CHMe}_2 \cdot \underset{\text{NMe}_3 \cdot \text{O} \cdot \text{CO} - \text{CH}_2}{\text{CH}} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \underset{\text{NMe}_3 \cdot \text{O} \cdot \text{CO} - \text{CH}_2}{\text{CHMe}}$ , is obtained. The *hydrochloride* melts at 191—192°.

[With L. FRESENIUS.]—An isomeric *betaine*,  $\text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \underset{\text{NMe}_3 \cdot \text{O} \cdot \text{CO} - \text{CH}_2}{\text{CHPr}}$ , may also be prepared from the aminodecoic acid obtained by the decomposition of tetrahydrocarvoneisooxime.

V. [With BÜCKER.]—By the reduction of phellandrene nitrite, prepared from water-fennel oil by Pesci's method with zinc and glacial acetic acid (*Gazzetta*, 1886, 16, 229), a *lævorotatory diamine* is obtained which boils at 250—253°, but resembles Pesci's diamine (b. p. 209—214°) in every other property. When phellandrene nitrite from *Eucalyptus amygdalina* is simply reduced, a *lævorotatory diamine* which is not identical with Pesci's is formed. It boils at 250—253° or at 132—134° under 17 mm. pressure, and is not readily volatile in steam. The *hydrochloride*,  $\text{C}_{10}\text{H}_{16}(\text{NH}_2)_2 \cdot \text{HCl}$ , or  $\text{C}_{10}\text{H}_{18}(\text{NH}_2)_2 \cdot \text{HCl}$ , melts at 209—210°, is not affected by exposure to air, is slightly soluble in cold alcohol, and on dry distillation yields cymene, ammonia, and ammonium chloride. The *platinichloride* is readily soluble in water. The phellandrenes obtained from different sources cannot, therefore, be identical, and the earlier formula for the nitrite containing the group  $\text{NO} \cdot \text{CH} \cdot \text{CHO} \cdot \text{NO}$  requires modification. E. W. W.

**Double Glucoside of Frangula Bark.** By E. AWENG (*Chem. Centr.*, 1902, ii, 147; from *Apoth. Zeit.*, 17, 372—373. Compare *Abstr.*, 1901, i, 39).—The original paper contains a detailed description of the preparation of the double glucoside of frangula bark in a state of purity, together with an account of its decomposition products and its relationship to  $\psi$ -frangulin and frangulic acid. E. W. W.

**Theory of the Dyeing Process.** By P. D. ZACHARIAS (*Chem. Zeit.*, 1902, 26, 680—681. Compare this vol., i, 635).—The dyeing process is governed by two phases: absorption and fixation. The colloidal nature of the fibre and the catalytic influence of the fibre on the formation of a colloidal precipitate must be taken into account. The equation given by Wegscheider (this vol., i, 635) should be  $dc/dx = d(c')/dx = 0$ , in the integration of the formula developed from Fick's law. The value of  $\nu$  may be greater than, equal to, or less than unity. J. McC.

**alloCinchonine.** By ARPÁD VON PECSICS (*Monatsh.*, 1902, 23, 443—454. Compare Hlavnička, *Abstr.*, 1901, i, 404).—When boiled with acetic anhydride, *allocinchonine* forms an *acetyl* derivative, which crystallises from light petroleum in white plates, sinters at 88°, melts at 92—94°, is easily soluble in alcohol, ether, benzene, or chloroform, and yields *allocinchonine* when hydrolysed by alcoholic potassium hydroxide. *Benzoylallocinchonine hydrochloride*, formed from *allocinchonine* and benzoyl chloride, is an amorphous powder; it melts at 230°, crystallises either from water in plates or from dilute alcohol in prisms which lose  $2\text{H}_2\text{O}$  at 105° and melt at 223°. The

*benzoyl* derivative crystallises from ether in short, white needles, melts at 118—119° and is hydrolysed by alcoholic potassium hydroxide to *allocinchonine* and benzoic acid. When acted on by phosphorus pentachloride in chloroform solution, *allocinchonine* yields *allocinchonine chloride*,  $C_{19}H_{21}N_2Cl$ . These reactions distinguish *allocinchonine* from  $\alpha$ - and  $\beta$ -*isocinchonine*, these bases giving negative results in the preceding experiments. These differences may be explained by assuming that *allocinchonine* contains a reactive hydroxyl group which is either absent in the molecules of its isomerides or marked by a different spacial configuration. With methyl iodide, *allocinchonine* forms a *methiodide*,  $C_{19}H_{22}ON_2, MeI, \frac{1}{2}H_2O$ , which crystallises in clusters of white needles, melts and decomposes at 245°, is easily soluble in hot water or ethyl alcohol, and sparingly so in methyl alcohol, and a *dimethiodide*,  $C_{19}H_{22}ON_2, 2MeI, 2H_2O$ , which crystallises in red needles or large, garnet-red monoclinic crystals, loses  $2H_2O$  at 105°, and melts at 235°. The methiodide forms a *hydriodide*,  $C_{19}H_{22}ON_2, MeI, HI$ , which crystallises in clusters of yellow plates, contains no water of crystallisation, and melts at about 232°, is easily soluble in hot water or alcohol, sparingly so in cold water or methyl alcohol, and gives a white, crystalline product on treatment with warm sodium carbonate solution.

*alloCinchonine hydriodide*,  $C_{19}H_{22}ON_2, HI, H_2O$ , crystallises in white prisms, is easily soluble in ethyl alcohol, sparingly so in methyl alcohol, and forms with methyl iodide a second *methiodide hydriodide*,  $C_{19}H_{22}ON_2, MeI, HI, \frac{1}{2}H_2O$ , which crystallises in glistening, lemon-yellow needles, loses  $\frac{1}{2}H_2O$  at 105°, melts at 250—253°, is easily soluble in ethyl alcohol, sparingly so in methyl alcohol, insoluble in ether, and on treatment with warm sodium carbonate solution yields a red, amorphous substance insoluble in ether. *alloCinchonine* must therefore be a di-tertiary base.

G. Y.

*alloCinchonine*. By ZDENKO HANNS SKRAUP and RUD. ZWERGER (*Monatsh.*, 1902, 23, 455—468. Compare preceding abstract).—*alloCinchonine* sulphate is oxidised by chromic acid to carbon dioxide, formic acid, acetic acid, cinchonic acid, kynurine, and *allomeroquinenine*; the last of these forms a *platinichloride*,  $(C_9H_{15}O_2N)_2, H_2PtCl_6, 3H_2O$ , crystallising from water in microscopic prisms which lose  $3H_2O$  at 110° and melt at 210—211°; a *hydrochloride*, which crystallises in clusters of needles, has a sp. gr. 1.0175, and  $[\alpha]_D - 114^\circ$ , and an *aureichloride*,  $C_9H_{15}O_2N, HAuCl_4$ , which crystallises in delicate needles, melts at 165—166°, is soluble in warm water, and is partly decomposed by boiling water.

*alloMeroquinenine* is isomeric with *meroquinenine* and with  $\beta$ -*isomeroquinenine* obtained by oxidation from *cinchonine* and also from  $\beta$ -*isocinchonine*. When heated with lime, it gives the same odour as is observed on similar treatment of *cincholeuonic acid*, *cincholeupon*, and  $\beta$ -*isomeroquinenine*, and when heated with zinc dust an oil having an odour resembling that of pyridine. The molecule of *allocinchonine* contains a quinoline nucleus and the remainder must be constituted similarly to that of *cinchonine*.

*Cincholeuonic acid* is not formed in the oxidation of *allocinchonine*,



as the part of the product insoluble in alcohol does not form an optically active hydrochloride.

On oxidation by potassium permanganate, *allocinchonine* sulphate yields formic acid and an amorphous substance resembling cinchonine.

Cinchonine and *allocinchonine* in sulphuric acid solution decolorise potassium permanganate, at first rapidly, the rate of oxidation gradually decreasing; with  $\alpha$ - and  $\beta$ -*isocinchonine*, the action is at first slow, increases in rapidity, and is accompanied by much frothing.  $\alpha$ - and  $\beta$ -*isocinchonine* are probably stereoisomerides of cinchonine and *allocinchonine*. G. Y.

**Correlation of the Constitution and Physiological Action of Morphine.** By ERNST VAHLEN (*Chem. Centr.*, 1902, i, 1302—1303; from *Arch. exp. Path. Pharm.*, 47, 368—410).—Since epiosine,

$$\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{NMe} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{C} \end{array} \text{---} \text{N} \text{---} \text{CH},$$
 has been found to possess physiological properties similar to those of morphine, the pharmacological action of the latter must be dependent on the presence of the phenanthrenoid group,
 
$$\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \text{---} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{C} \text{---} \text{N} \end{array}.$$

*Morphigenine hydrochloride*,  $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{OH} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{NH}_2 \end{array} \cdot \text{HCl}$ , prepared by reducing phenanthraquinone hydrazone with stannous chloride, crystallises in coloured needles, becomes reddish at 180°, but does not melt at 290°, is decomposed by water, especially on heating, and is readily soluble in boiling glacial acetic acid or in hot concentrated hydrochloric acid, but only slightly so in the cold solvents. By the action of alkali hydroxides or carbonates on the hydrochloride, phenanthraquinone is regenerated. By the action of zinc chloride on morphigenine hydrochloride, products were obtained which were not isolated, but their aqueous solutions had a distinct narcotic effect on dogs and frogs. Epiosine, prepared by the action of methylamine on morphigenine hydrochloride, was found to be identical with Japp and Davison's *N*-methylphenyleneimidazole (*Trans.*, 1895, 67, 32); it melts at 195°. The physiological actions of morphigenine hydrochloride and epiosine are described in detail in the original paper. E. W. W.

**2-Cyanopyridine.** By HANS MEYER (*Monatsh.*, 1902, 23, 437—442. Compare *Abstr.*, 1901, i, 407).—Picolinamide is best prepared by the action of aqueous ammonia on picoliny chloride and extraction with chloroform. In the preparation of the amide from the ester, the solution of the hydrochloride from the latter, obtained by passing hydrogen chloride into an absolute alcoholic solution of picolinic acid, is concentrated and shaken with aqueous ammonia (compare *Abstr.*, 1894, i, 425, 472).

*2-Cyanopyridine*, prepared by the action of thionyl chloride on picolinamide at 90—100°, crystallises from ether in long, colourless needles, melts at 26°, is slightly volatile at the ordinary temperature, boils at 212—215°, has an intense odour resembling those of benz-

aldehyde and of coumarin, and is easily soluble in water, alcohol, ether, or chloroform. It has slight basic properties and forms an orange-red, crystalline *platinichloride*,  $(C_6H_4N_2)_2, H_2PtCl_6$ , and an *aurichloride*,  $C_6H_4N_2, HAuCl_4$ , which crystallises in lemon-yellow needles, losing about  $1H_2O$  and becoming opaque at  $100^\circ$ ; it melts at  $190^\circ$  and is sparingly soluble in water, dissolving easily in dilute hydrochloric acid.

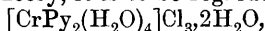
Picolinic acid forms an *aurichloride* which crystallises in glistening, straw-yellow leaflets, melts at  $200^\circ$ , decomposes with evolution of gas at  $204^\circ$ , and is easily soluble in water.

*Picolinamide aurichloride* is an insoluble, light yellow, crystalline powder which sinters at about  $215^\circ$ , but melts only at a much higher temperature. The *aurichloride* of 2-aminopyridine crystallises from concentrated hydrochloric acid in long, glistening, garnet-red needles and melts at  $231^\circ$ . 2-Cyanopyridine is hydrolysed by concentrated hydrochloric acid at  $120^\circ$ , giving a quantitative yield of ammonia and picolinic acid.

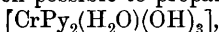
G. Y.

**Tetra-aquodipyridinechromium Salts.** By PAUL PFEIFFER (*Zeit. anorg. Chem.*, 1902, 31, 401—436).—Werner's theory connecting the metal-ammonia compounds and salt hydrates is supported by the facts now known about the intermediate products. The author has investigated some of these intermediate products containing pyridine in place of ammonia. [In the formulæ given  $Py = C_5NH_5$ .]

The chloride,  $CrCl_3, 2Py, 6H_2O$ , loses 2 mols. of water in a desiccator containing phosphoric oxide and gives  $CrCl_3, 2Py, 4H_2O$ ; therefore, according to Werner's theory, it is to be regarded as

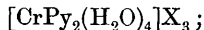


and is consequently an intermediate product between  $[CrPy_6]Cl_3$  and  $[Cr(H_2O)_6]Cl_3$ . In aqueous solution, all the chlorine is ionised and it undergoes metathetical reactions. Like the pure hydrates, it gives basic salts such as  $[CrPy_2(H_2O)_2(OH)_2]Cl$  when hydroxides are added. The salts are all red, crystallise well from water, and the aqueous solutions have an acid reaction. When heated, they give off pyridine and become green. The basic salts dissolve in acids, giving red solutions. It has not been possible to prepare the free base,

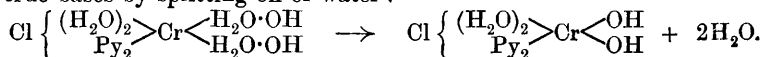


because the basic salts dissolve in alkalis or ammonia.

The author has already introduced a slight modification (*Naturwiss. Rundsch.*, 1901, 366) into Werner's theory. According to the proposition suggested, a definite place in the molecule is assigned to the negative radicle. For the tetra-aquodipyridinechromium salts, the formula  $X \left\{ \begin{array}{c} (H_2O)_2 \\ Py_2 \end{array} \right\} Cr \left\langle \begin{array}{c} H_2OX \\ H_2OX \end{array} \right\rangle$  is given, indicating that the position of one X is uncertain. This shows that these are oxonium salts. The properties of the hydroxylopyridine salts which have been obtained indicate that they are not the basic salts corresponding with



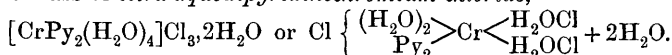
they are rather to be regarded as salts of pseudo-bases formed from the true bases by splitting off of water:



The idea of pseudo-salts can also be advantageously applied to metal-ammonia compounds.

The starting point for the preparation of the tetra-aquodipyridine-chromium salts is *diaquodihydroxylodipyridinechromium chloride*,  $[\text{CrPy}_2(\text{OH})_2(\text{H}_2\text{O})_2]\text{Cl}$ , which is obtained from green chromic chloride hexahydrate,  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ , by the action of pyridine; it may be prepared in like manner from the double salt,  $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 2\text{HClPy}$ , which is most easily obtained by adding successively pyridine and a large excess of concentrated hydrochloric acid to a solution of chromic chloride; a third method of preparation is by warming  $\text{CrCl}_3\text{Py}_3$  with a 10 per cent. solution of ethylenediamine. The diaquo-salt is obtained in fine needles which decompose at  $100^\circ$ ; it is quite insoluble in the ordinary solvents, but can be recrystallised from pyridine.

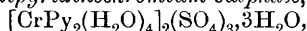
When the dihydroxylochloride is treated with concentrated hydrochloric acid, the greenish-grey compound is converted into a red, crystalline mass of *tetra-aquodipyridinechromium chloride*,



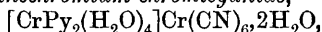
This is very easily soluble in water, ethyl alcohol, or methyl alcohol, but insoluble in ether, acetonitrile, acetic acetate, acetic acid, or chloroform. The aqueous solution remains unchanged at the ordinary temperature, but decomposition occurs when it is heated on the water-bath. The red, alcoholic solution quickly decomposes and deposits the greenish, basic chloride. The reactions with various reagents have been studied. In the air, the salt is converted into the greenish-violet *hydroxylotriaquodipyridinechromium chloride*,  $[\text{CrPy}_2(\text{H}_2\text{O})_3\text{OH}]\text{Cl}_2$ .

*Tetra-aquodipyridinechromium bromide*,  $[\text{CrPy}_2(\text{H}_2\text{O})_4]\text{Br}_3 \cdot 2\text{H}_2\text{O}$ , obtained from the dihydroxylochloride, or the normal chloride, by solution in concentrated hydrobromic acid, separates in red crystals from concentrated hydrobromic acid solution. It closely resembles the chloride but is rather more stable. *Dihydroxylodiaquodipyridinechromium bromide*,  $[\text{CrPy}_2(\text{H}_2\text{O})_2(\text{OH})_2]\text{Br}$ , is almost quantitatively precipitated by the addition of pyridine to a solution of the normal bromide; it has a greenish tinge and is decomposed on heating.

When the dihydroxylochloride is rubbed with sulphuric acid, a red solution is produced from which flat, red needles of *tetra-aquodipyridinechromium hydrogen sulphate*,  $\text{SO}_4[\text{CrPy}_2(\text{H}_2\text{O})_4]\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , separate. The salt is very easily soluble in water and the solution has an acid reaction; it is insoluble in alcohol or ether. When alcohol is added to the concentrated aqueous solution of this salt, violet crystals of *tetra-aquodipyridinechromium sulphate*,



are formed. This sulphate remains unchanged in the air, but is decomposed by water; when placed beside phosphoric oxide, it does not lose in weight. When a solution of the tetra-aquo hydrogen sulphate is precipitated with pyridine, fine, greyish-blue crystals of *hydroxylotriaquodipyridinechromium sulphate*,  $[\text{CrPy}_2(\text{H}_2\text{O})_3(\text{OH})]\text{SO}_4$ , separate; the latter salt is soluble in much water to a greenish solution having a neutral reaction.

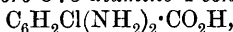
*Tetra-aquodipyridinechromium chromicyanide,*

is precipitated when potassium chromicyanide is added to a solution of the tetra-aquochloride containing some hydrochloric acid. It is obtained in red plates which are insoluble in water. J. McC.

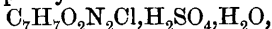
**Hydroxypyrazolone Derivatives of the Naphthalene Series.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 131537).—The hydrazine derivative obtained from 7-amino- $\alpha$ -naphthol-3-sulphonic acid, when condensed with ethyl acetoacetate in the presence of dilute acetic acid, gives rise to hydroxypyrazolonesulphonic acid, which separates in granular crystals when the mixture is treated with excess of hydrochloric acid. This product yields a yellow *nitroso*-derivative.

Other hydrazines of the naphthalene series may be employed in this condensation and the reaction also occurs with ethyl oxaloacetate or dihydroxytartaric acid. G. T. M.

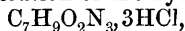
**Chloro-*m*-phenylenediaminecarboxylic Acid.** By PAUL COHN and MARKUS SCHIFFERES (*Chem. Centr.*, 1902, i, 1293; from *Zeit. Farben- Textil-Chem.*, 1902, 1, 205—206).—4-Chloro-*m*-phenylenediamine-5-carboxylic acid or 2-chloro-3:5-diamino-1-benzoic acid,



prepared by reducing 2-chloro-3:5-dinitrobenzoic acid with stannous chloride and hydrochloric acid, is very readily soluble in water and was not isolated. The *hydrochloride*,  $\text{C}_7\text{H}_7\text{O}_2\text{N}_2\text{Cl} \cdot 2\text{HCl}$ , crystallises from alcohol in small, pale yellow needles. The *sulphate*,



was also prepared. The *diacetyl* derivative,  $\text{C}_6\text{H}_2\text{Cl}(\text{NHAc})_2 \cdot \text{CO}_2\text{H}$ , crystallises from water in needles and melts at 288—289°. 2-Amino-3:5-dinitrobenzoic acid, on reduction with stannous chloride and hydrochloric acid, forms 2:3:5-triaminobenzoic acid. The free acid prepared by treating the solution of the hydrochloride,



with sodium acetate quickly becomes red. The sulphate forms brownish-yellow needles and is almost insoluble in water. E. W. W.

**3-Amino-4-methylpheno- $\beta$ -naphthacridine.** FRITZ ULLMAN (D.R.-P. 130943).—3-Amino-4-methylpheno- $\beta$ -naphthacridine, formerly obtained by condensing 2:4:2':4'-tetra-amino-3:3'-ditolylmethane with  $\beta$ -naphthol, is now prepared by heating the latter compound at 200° with the product,  $\text{C}_8\text{H}_{10}\text{N}_2$ , formed by the interaction of formaldehyde and tolylene-2:4-diamine in molecular proportion, the reaction being effected in neutral solutions. G. T. M.

**Proteids of Yeast.** By R. SCHRÖDER (*Beitr. chem. Physiol. Path.*, 1902, 2, 389—403).—The proteid substance, which can be obtained from yeast by treatment with ether and water, and can be precipitated from this solution by heating, gives all the proteid reactions; the lead reaction is feeble. By decomposition with acids, it yields leucine, tyrosine, phenylalanine, and bases. The bases contain about a quarter of its total nitrogen, and of them lysine is the most abundant. A

part of the sulphur is present in a cystin-like combination. The question of a carbohydrate group is left for future consideration.

W. D. H.

**Melanins which Originate from Proteid.** By FRANZ SAMUELY (*Beitr. chem. Physiol. Path.*, 1902, 2, 355—388).—The ill-characterised and probably numerous substances, named melanins and melanoidins, can be artificially prepared from proteids. In their formation, the tyrosine group, and especially the heterocyclic nucleus (pyrrole, pyridine, skatole) of the proteid appears to be important. The relationship of these substances to humin is discussed.

W. D. H.

**The Albumose Precipitates produced by Papain and Rennin (Coaguloses and Plasteins).** By D. KURAÉEFF (*Beitr. chem. Physiol. Path.*, 1902, 2, 411—424).—The precipitates produced by adding rennin and papain to various albumoses and caseoses were examined and analysed. These substances are probably closely related to anti-albumid, and possibly to bacterial coagulins. These are characterised by a high percentage of carbon and a low percentage of nitrogen, so differing from the proteoses.

W. D. H.

**Decomposition of Proteids.** By H. STEUDEL (*Zeit. physiol. Chem.*, 1902, 35, 540—544).—The usual method of obtaining hexon bases from proteids is by means of mineral acid. If boiling baryta water is used instead, the proportion of the bases is different, lysine being by far the most abundant. Whether this is due to the destruction of the other bases during the boiling is uncertain. The decomposition of proteids produced by ferments is very similar to that produced by baryta.

W. D. H.

**The Nucleo-proteid of the Suprarenal Gland.** By WALTER JONES and G. H. WHIPPLE (*Amer. J. Physiol.*, 1902, 7, 423—434).—This substance is not a nucleo-histon, and its composition is identical whether prepared from the ox or sheep. It is closely similar to that obtained from the pancreas. On decomposition, it yields guanine and adenine in the same relative proportion. Xanthine, hypoxanthine, and epiguanine are either absent or present in the merest traces. As these three bases were found by Okerblom (*Abstr.*, 1899, ii, 778) in suprarenal extracts, there is an interesting and curious difference between the bases preformed in the gland and those which result from the hydrolytic decomposition of its nucleo-proteid.

W. D. H.

**The Constitution of Proteid Cystin.** By ERNST FRIEDMANN (*Beitr. chem. Physiol. Path.*, 1902, 2, 433—434).—The older physiologists regarded the sulphur-containing complex in a proteid as the source of taurine. Recent research has shown that the sulphur-group of proteid is cystin or cystein. The possibility of its transformation into taurine is excluded if Baumann is correct in considering that cystein is  $\alpha$ -aminothiolactic acid,  $\text{SH} \cdot \text{CMe}(\text{NH}_2) \cdot \text{CO}_2\text{H}$ .

The present research shows that the cystin from proteid is different from ordinary cystin. Proteid cystein is a compound of  $\beta$ -thiolactic acid,  $\text{SH} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$ . By the usual treatment, this

can be changed into cysteic acid (aminosulphopropionic acid),  $\text{SO}_3\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ , and from this, by the loss of carbon dioxide, taurine,  $\text{SO}_3\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ , is obtained.

Proteid cystein is thus a derivative of glyceric acid, not, as with mercapturic acid cystein, of pyruvic acid, and stands in close relationship to serin.

W. D. H.

**Action of Iodine on Proteids. I.** By C. H. L. SCHMIDT (*Zeit. physiol. Chem.*, 1902, **35**, 386—395. Compare this vol., i, 251).—The amount of amic nitrogen eliminated from the proteid molecule during iodination is a function of the concentration of the iodine solution used; the more concentrated the solution, the greater is the amount of iodide and iodate formed and the less that of hydriodic acid.

J. J. S.

**Experiments on Malt Diastase.** By ARTHUR R. LING and BERNARD F. DAVIS (*J. Fed. Inst. Brewing*, 1902, **8**, 475—495).—When diastase from well-grown, low-dried malt is allowed to act on starch paste of 2—5 per cent. strength at 50—60°, the starch is hydrolysed in about 1½ hours to a point at which  $[\alpha]_{\text{D}}^{39.93}$  is 149.5—150° and the cupric reducing power  $\text{R}_{3.93}$  is 77—78, whilst after 42 hours these constants are substantially those of maltose, and in such a solution nothing but maltose can be detected. Diastase prepared from malt grown under abnormal conditions (such as small quantities prepared in the laboratory) and diastase which has been slowly heated to 115—120° do not hydrolyse the starch completely to maltose, even if allowed to act in large excess; diastase which has been rapidly heated to 115—120° produces a more pronounced effect.

Neither the final temperature at which a sample of malt has been kilned (considered alone), nor the “diastatic power” determined in accordance with Kjeldahl’s “law of proportionality” by Lintner’s method, is a criterion of its behaviour towards starch. When a diastase solution is heated above 65°, its reaction with starch paste appears to be quite different to that of a solution which has not been heated above 60°; this is shown, not only by the specific rotatory and cupric reducing power of the dissolved matter, but also by the presence of dextrose among the final products of hydrolysis.

E. G.

**Catalase.** By OSCAR LOEW (*Zeit. Biol.*, 1902, **43**, 256—257).—The ferment in milk which causes decomposition of hydrogen peroxide has been termed superoxydase by Raudnitz. It is identical with the ferment previously named catalase by the author (*Abstr.*, 1901, i, 435).

W. D. H.

## Organic Chemistry.

**Composition of Petroleum. Hydrocarbons in Pennsylvania Petroleum with Boiling Points above 216°.** By CHARLES F. MABERY (*Amer. Chem. J.*, 1902, 28, 165—198).—The following hydrocarbons have been isolated from the fractions of Pennsylvania petroleum boiling above 216°; they were purified by treatment with fuming sulphuric acid.

Tridecane,  $C_{13}H_{28}$ , boils at 221—222° and has a sp. gr. 0.7834 and  $n_D$  1.4354 at 20°; its *chloro*-derivative,  $C_{13}H_{27}Cl$ , boils at 135—140° under 12 mm. pressure and has a sp. gr. 0.8973 and  $n_D$  1.451 at 20°.

Tetradecane,  $C_{14}H_{30}$ , boils at 142—143° under 50 mm. and at 236—238° under 760 mm. pressure and has a sp. gr. 0.7814 and  $n_D$  1.4360 at 20°; its *chloro*-derivative,  $C_{14}H_{29}Cl$ , boils at 150—153° under 20 mm. pressure, and has a sp. gr. 0.9185; the *dichloro*-derivative,  $C_{14}H_{28}Cl_2$ , boils at 175—180° under 12 mm. pressure and has a sp. gr. 1.032 at 20°.

Pentadecane,  $C_{15}H_{32}$ , boils at 158—159° under 50 mm. and at 256—257° under 760 mm. pressure and has a sp. gr. 0.7896 and  $n_D$  1.4413 at 20°; the *dichloro*-derivative,  $C_{15}H_{30}Cl_2$ , boils at 175—180° under 13 mm. pressure and has a sp. gr. 1.0045 at 20°.

Hexadecane,  $C_{16}H_{34}$ , boils at 174—175° under 50 mm. and at 275—276° under 760 mm. pressure and has a sp. gr. 0.7911 and  $n_D$  1.4413 at 20°; the *dichloro*-derivative,  $C_{16}H_{32}Cl_2$ , boils at 205—210° under 16 mm. pressure and has a sp. gr. 1.0314 at 20°.

Heptadecane,  $C_{17}H_{36}$ , boils at 188—190° under 50 mm. and at 288—289° under 760 mm. pressure and has a sp. gr. 0.8000 at 20°; the *chloro*-derivative,  $C_{17}H_{35}Cl$ , boils at 175—177° under 15 mm. pressure and has a sp. gr. 0.8962 at 20°.

The fraction which boiled at 199—200° under 50 mm. and at 300—301° under 760 mm. pressure had a sp. gr. 0.8017 at 20° and furnished a *chloro*-derivative,  $C_{18}H_{37}Cl$ , which boiled at 185—190° under 15 mm. pressure and had a sp. gr. 0.9041 at 20°. When this fraction was cooled to -10°, a white, solid octodecane,  $C_{18}H_{38}$ , separated, which melts at 20° and has a sp. gr. 0.7830 at 20°/20° and 0.7816 at 40°/20°, and  $n_D$  1.440. After the solid hydrocarbon had been removed by filtration, the liquid portion had a sp. gr. 0.8110 at 20°,  $n_D$  1.4435, and a composition indicating that it was a mixture of the two hydrocarbons,  $C_{18}H_{38}$  and  $C_{18}H_{36}$ .

The fraction boiling at 210—212° under 50 mm. pressure had a sp. gr. 0.8122 and  $n_D$  1.4522 at 20°. On cooling this fraction to -10°, solid nonodecane,  $C_{19}H_{40}$ , separated, which melts at 33—34° and has a sp. gr. 0.7725 at 30°/30° and 0.7781 at 40°/30°; the filtered oil had the composition  $C_{19}H_{38}$ , a sp. gr. 0.8208, and  $n_D$  1.4515 at 20°.

The distillate collected at 230—232° under 50 mm. pressure had a sp. gr. 0.8230 and  $n_D$  1.4608 at 20°; it consisted of a solid heneicosane,

$C_{21}H_{44}$ , melting at  $40-41^\circ$ , and a liquid hydrocarbon,  $C_{21}H_{42}$ , which has a sp. gr. 0.8424 at  $20^\circ$ .

The fraction boiling at  $240-242^\circ$  under 50 mm. pressure had a sp. gr. 0.8230 and  $n_D$  1.454 at  $20^\circ$ . On cooling, it deposited a solid docosane,  $C_{22}H_{46}$ , which melts at  $44^\circ$  and has a sp. gr. 0.7796 at  $60^\circ$ ; the liquid portion,  $C_{22}H_{44}$ , had a sp. gr. 0.8296 at  $20^\circ$ .

The portion collected at  $258-260^\circ$  under 50 mm. pressure had a sp. gr. 0.8341 at  $60^\circ$ , 0.8320 at  $70^\circ$ , and 0.8310 at  $80^\circ$ . It furnished a small proportion of a solid tricosane,  $C_{23}H_{48}$ , which melts at  $45^\circ$  and has a sp. gr. 0.7894—0.7900 at  $60^\circ$ ; the filtered liquid,  $C_{23}H_{46}$ , had a sp. gr. 0.8569 and  $n_D$  1.4714 at  $20^\circ$ .

The distillate, at  $272-274^\circ$  under 50 mm. pressure, consisted of a solid tetracosane,  $C_{24}H_{50}$ , which melts at  $48^\circ$  and has a sp. gr. 0.7902 at  $60^\circ$ , 0.7893 at  $70^\circ$ , and 0.7875 at  $80^\circ$ , and a liquid hydrocarbon,  $C_{24}H_{48}$ , which has a sp. gr. 0.8582 at  $40/20^\circ$  and  $n_D$  1.4726.

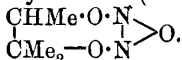
The fraction boiling at  $280-282^\circ$  under 50 mm. pressure yielded a solid pentacosane,  $C_{25}H_{52}$ , which crystallises in plates and melts at  $53-54^\circ$ ; the liquid portion,  $C_{26}H_{52}$ , had a sp. gr. 0.8580 and  $n_D$  1.4725.

The portion collected at  $292-294^\circ$  under 50 mm. pressure was composed of a solid hexacosane,  $C_{26}H_{54}$ , melting at  $58^\circ$ , and a thick, viscous oil,  $C_{27}H_{52}$ , which had a sp. gr. 0.8688 at  $26^\circ$  and  $n_D$  1.4722.

The distillate, at  $310-312^\circ$  under 50 mm. pressure, furnished a solid octocosane,  $C_{28}H_{58}$ , which melted at  $60^\circ$  and had a sp. gr. 0.7945 at  $70^\circ$ , 0.7927 at  $80^\circ$ , and 0.7911 at  $90^\circ$ , and a thick oil,  $C_{28}H_{54}$ , which had a sp. gr. 0.8694 and  $n_D$  1.480.

E. G.

**Desmotropism of Trimethylethylene Nitrosite.** By ARTHUR HANTZSCH (*Ber.*, 1902, **35**, 2978—2980).—A discussion of the constitution of the additive product of nitrogen trioxide and  $\beta$ -methyl- $\Delta^2$ -butylene described by Schmidt (this vol., i, 581), for which the author prefers the formula



R. H. P.

**Connection between Bisnitrosyl Compounds and Nitroso-compounds.** By OSCAR PILOTY (*Ber.*, 1902, **35**, 3090—3093).—Comparing the properties of the nitroso-compounds described in the two following papers, the author concludes that there is no essential difference between nitroso-compounds and the bisnitrosyl compounds which contain the  $N_2O_2$  group. On the contrary, the transition from the one class to the other is gradual; the typical nitroso-compounds are unimolecular liquids or crystallised solids of a deep blue colour; some nitroso-compounds form colourless solids which become blue when melted or dissolved, and these are bimolecular in the cold and contain the  $N_2O_2$  group. The difficulty of resolving the  $N_2O_2$  group into two NO groups increases until finally the typical bisnitrosyl compounds are arrived at, and these no longer show the blue colour under any conditions.

J. McC.

**Constitution of  $\psi$ -Nitroles and some Bromonitrosohydrocarbons.** By OSCAR PILOTY and A. STOCK (*Ber.*, 1902, **35**, 3093—3101).—*Propyl- $\psi$ -nitrole*, prepared from  $\beta$ -bromo- $\beta$ -nitrosopropane by shaking



in ethereal solution with silver nitrite, forms white crystals which melt at  $76^{\circ}$ .

$\beta$ -Bromo- $\beta$ -nitrosobutane, formed when methylethylketoxime in aqueous solution is treated with bromine in presence of pyridine, is a deep blue, volatile liquid which boils at  $28^{\circ}$  under 19 mm. pressure and has a sp. gr. 1.360 at  $22^{\circ}$ . With silver nitrite, it gives *butyl- $\psi$ -nitrole*, which melts at  $58^{\circ}$ .

In the same way, from diethylketoxime,  $\beta$ -bromo- $\beta$ -nitrosopentane is formed as a liquid which boils at  $49^{\circ}$  under 17 mm. pressure and has a sp. gr. 1.325 at  $20^{\circ}$ ; with silver nitrite, it gives *amyl- $\psi$ -nitrole* melting at  $63.5^{\circ}$ .

By the action of bromine in presence of pyridine on the oxime obtained by treating pinacolin with hydroxylamine,  $\gamma$ -bromo- $\gamma$ -nitroso- $\beta\beta$ -dimethylbutane is produced. It forms volatile, blue crystals with an odour recalling that of camphor.

The formation of bromonitroso-compounds is a useful test for ketones. The solution to be tested should be made neutral, and to it a drop of a 10 per cent. solution of hydroxylamine hydrochloride and one of a 5 per cent. solution of sodium hydroxide added. A large drop of pyridine is introduced and a thin layer of ether poured on, after which it is shaken with sufficient bromine to impart a yellow colour to the ether. If, on addition of hydrogen peroxide, the ether becomes blue, the presence of a ketone or ketonic group may be concluded.

When *butyl- $\psi$ -nitrole* is dissolved in anhydrous hydrogen cyanide at  $-10^{\circ}$ , the solution is colourless; the depression of the freezing point of the hydrogen cyanide was observed, and again, after standing, when the solution had become quite blue. It was found that the second depression was exactly double the first, indicating that in the colourless form the  $\psi$ -nitrole has a doubled molecular formula.

From the transformation of the bromonitroso-compounds into  $\psi$ -nitroles with silver nitrite, the authors conclude that the former are true nitroso-compounds.

J. McC.

**Halogenated Nitroso-compounds of Diketocyclohexamethylene and a Secondary Nitroso-compound.** By OSCAR PILOTY and HERMANN STEINBOCK (*Ber.*, 1902, 35, 3101—3117).—By the action of bromine, in presence of pyridine, on the dioxime of *p*-diketocyclohexane, 1:4-dibromo-1:4-dinitrosocyclohexane is formed; it crystallises in deep blue, rhombic pyramids, melts at  $89^{\circ}$ , and is very easily soluble in alcohol, acetic acid, ether, or benzene. In this reaction, it is the *cis-trans*-modification which is formed, and there is also produced 1:4-dibromo-1:4-bisnitrosocyclohexane which is colourless and insoluble in ether. Nitric acid or chromic and acetic acids transform the nitroso-compound into 1:4-dibromo-1:4-dinitrocyclohexane, which melts at  $158^{\circ}$  and is insoluble in water, but easily soluble in alcohol, ether, or acetic acid.

When a current of chlorine is passed through a cooled hydrochloric acid solution of *p*-diketocyclohexanedioxime, the *cis-trans*-modification of 1:4-dichloro-1:4-dinitrosocyclohexane is produced. It is formed much more easily than the corresponding bromo-compound and does not require the presence of pyridine. It forms deep blue, monoclinic

prisms, melts at  $108.5^{\circ}$ , and is easily soluble in the common organic solvents. When hydrogen chloride is passed through a solution of it in glacial acetic acid, it changes into 1:4-dichloro-1:4-bisnitrosylcyclohexane, which separates in colourless crystals. This represents a new class of intermolecular bisnitrosyl compounds for which the formula

developed is  $\text{CCl} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{N}_2\text{O}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{CCl}$ . It is soluble in methyl alcohol,

acetone, or acetic acid to a colourless solution which, when heated, becomes blue, and again colourless when cooled. This characteristic reaction is attributed to its conversion into a nitroso-compound at the higher temperature. With chromic and acetic acids, the chloronitroso-compound gives 1:4-dichloro-1:4-dinitrocyclohexane as a greenish substance which melts at  $178^{\circ}$  and is soluble in the ordinary organic solvents.

By the action of chlorine on benzaldoxime, a very unstable, blue substance is formed which the authors believe to be *o*-chloro-*o*-nitrosotoluene,  $\text{CHPhCl}\cdot\text{NO}$ .

With acetaldoxime in hydrochloric acid solution, chlorine gives *monochloronitrosoethane*, which can be obtained in colourless plates; it dissolves in ether or methyl alcohol with a deep blue colour and melts at  $65^{\circ}$  to a blue liquid which becomes colourless on solidifying. It is spontaneously transformed into acetohydroxamic acid chloride ( $\text{CHMeCl}\cdot\text{NO} \rightarrow \text{CMeCl}\cdot\text{N}\cdot\text{OH}$ ), which solidifies at  $-3^{\circ}$ . When dissolved in hydrochloric acid and treated with chlorine, this hydroxamic acid chloride gives *dichloronitrosoethane*,  $\text{CH}_3\cdot\text{CCl}_2\cdot\text{NO}$ , as a liquid which boils at  $68^{\circ}$ (corr.); it is miscible with alcohol, ether, or benzene, but not with water, and has a sp. gr. 1.2521 at  $19^{\circ}$ .

The constant for the molecular depression of the freezing point of anhydrous hydrogen cyanide has been determined to be 21.7, and a normal molecular weight has been found for dichloronitrosoethane in this solvent.

J. McC.

**Formation of Alcohols by the Electrolysis of the Salts of the Fatty Acids.** By HANS HOFER and M. MOEST (*Annalen*, 1902, 323, 284—323).—Methyl alcohol is produced when sodium acetate is electrolysed in aqueous solutions containing sodium perchlorate; under similar conditions, the corresponding propionate and *n*- and *iso*-butyrates give rise to ethyl and *n*- and *iso*-propyl alcohols respectively. Sodium succinate yields hydracrylic acid instead of ethylene glycol. Other inorganic salts induce this reaction, namely, chlorates, sulphates, carbonates, and hydrogen carbonates. The aldehydes corresponding with the alcohols are also formed during the electrolysis. Only small quantities of the alcohols and aldehydes are obtained on electrolysing valerates and hexoates.

The communication includes a detailed account of the apparatus employed and tables indicating the composition of the gases produced with solutions of varying concentration (compare Abstr., 1894, i, 228; 1896, i, 10, 664).

G. T. M.

**Action of Alcohols on Esters.** By LOUIS HENRY (*Bull. Acad. Roy. Belg.*, 1902, 445—494).—The action of alcohols on esters is not

dependent simply on the reactive intensity of the alcohol (measured by its esterification velocity for acetic acid) except in the cases of the action of methyl or ethyl alcohol on amyl, glyceryl, and cellulose nitrites (compare Bertoni, Abstr., 1886, 217, and 1887, 458) and of the same alcohols on mixed acid anhydrides (compare Behal, Abstr., 1899, i, 734), which the author regards as a class of esters.

In many cases, the action is modified by the reactive intensity of the acid residue of the ester, thus, pyruvyl formate,  $\text{CH}_3\text{Ac}\cdot\text{O}\cdot\text{CHO}$ , is decomposed by methyl alcohol with the liberation of pyruvyl alcohol (a small amount of the corresponding ether melting at  $130^\circ$  is also formed), whilst pyruvyl acetate is not attacked.

Temperature is also an important factor, thus, whilst amyl nitrite is decomposed in the cold by methyl or ethyl alcohol, it is not attacked by propyl or butyl alcohol until heated, although these possess higher reactive intensities than amyl alcohol. In some cases, the effect of temperature is to invert the action altogether, thus: glycol, when boiled with diethyl succinate, liberates ethyl alcohol, although the reactive intensities of the two alcohols are respectively 66.5 and 53.9, the abnormality being due to the greater volatility of ethyl alcohol (compare Vorländer, Abstr., 1895, i, 17).

It is probable also that solubility plays a considerable part in influencing actions of this type.

Functional inertia of the alcohol may also be overcome by greatly increasing its reacting mass, relatively to that of the ester (compare Walker, Abstr., 1893, i, 500, and Vorländer, *loc. cit.*).

Reactive intensity in a homologous series of alcohols decreases as the series is ascended, and the same result is produced by the introduction of negative groups such as OH, Cl, CO, the effects of these increasing with their proximity to the original OH group of the alcohol (compare Heintz, *Annalen*, 1861, 114, 440; Bertoni, *loc. cit.*; Richter, this Journal, 1877, ii, 439; Rose, Abstr., 1881, 251; Bachmann, Abstr., 1883, 726; Behal, *loc. cit.*; Henry, Abstr., 1901, i, 577; Vorländer, *loc. cit.*), where reactions illustrating this general statement are to be found. In the original paper, explanations of these reactions embodying the foregoing views are given.

T. A. H.

**Mono-ethers of Bivalent Alcohols.** By M. H. PALOMAA (*Ber.*, 1902, 35, 3299—3301).—By treating ethylene glycol with sodium and an alkyl iodide, the mono-ethers are obtained. *Glycol monomethyl ether*,  $\text{OMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , boils at  $124\text{--}125^\circ$ , has an ethereal odour and a sp. gr. 0.9703 at  $19^\circ/19^\circ$ , and is miscible with water. With acetic anhydride, it gives an *acetate* of the formula  $\text{OMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OAc}$ , which boils at  $144.5\text{--}145^\circ$  and has a sp. gr. 1.0090 at  $19^\circ/19^\circ$ .

The *mono-n-propyl ether of ethylene glycol*,  $\text{Pr}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , boils at  $152\text{--}153^\circ$  and has a sweet odour and a sp. gr. 0.9159 at  $19^\circ/19^\circ$ .

J. McC.

**Products which are Formed by simultaneously passing Dry Sulphur Dioxide and Ammonia into Absolute Alcohol distilled over Sodium.** By ALWIN GOLDBERG and M. R. ZIMMERMANN (*Zeit. angew. Chem.*, 1902, 15, 898—906).—The ammonium sulphites,

obtained by passing sulphur dioxide and ammonia into absolute alcohol, were first prepared by Muspratt (*Annalen*, 1844, 50, 269), and subsequently studied in detail by Schumann (*Abstr.*, 1900, ii, 271). Divers (*Trans.*, 1899, 75, 533) prepared ammonium ethyl sulphite by using carefully dried alcohol and a low temperature,  $-15^{\circ}$ . The authors have prepared the same compound, which they call *ammonium ethoxysulphinate*, at the ordinary temperature; it is decomposed by hot water into ammonium pyrosulphite and alcohol. *Ammonium methoxysulphinate*,  $\text{OMe}\cdot\text{SO}\cdot\text{ONH}_4$ , is prepared similarly, as are also the analogous derivatives of amyl alcohol, methylethylcarbinol, and trimethylcarbinol. The compound from allyl alcohol is formed by union of 3 mols. of ammonia and sulphur dioxide respectively, and 2 mols. of allyl alcohol; from the fact that only two-thirds of the sulphur dioxide can be titrated by iodine, the salt is represented by the formula  $\text{ONH}_4\cdot\text{SO}\cdot\text{O}\cdot[\text{CH}_2]_3\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}\cdot\text{ONH}_4$ .

On leading ammonia into molten ammonium ethyl sulphite at  $99^{\circ}$ , *ammonium aminosulphinate*,  $\text{NH}_2\cdot\text{SO}\cdot\text{ONH}_4$ , is formed. When ammonium ethyl sulphite is heated, ammonium sulphate is formed; when heated under pressure with absolute alcohol or ethyl bromide, ammonium sulphate and thiosulphate are produced; if the salt is heated alone under pressure, besides ammonium sulphate and sulphur, a yellow oil,  $\text{C}_4\text{H}_{10}\text{O}_4\text{S}_3$ , which is volatile with steam, is obtained. Ammonium methyl sulphite decomposes in a similar manner. K. J. P. O.

**Action of Acid Chlorides and Anhydrides of the Fatty Series on Trioxymethylene.** By MARCEL DESCUDÉ (*Bull. Soc. Chim.*, 1902, [iii], 27, 867—871. Compare *Abstr.*, 1901, i, 644, and this vol., i, 149, 339, 451).—When trioxymethylene reacts with acetyl chloride in presence of zinc chloride, there are formed chloromethyl acetate, dichloromethyl oxide, and methylene diacetate; the last, which boils at  $170^{\circ}$ , is also formed by the action of acetic anhydride on trioxymethylene in presence of zinc chloride. In this reaction, there is also produced *methyleneoxide diacetate*,  $(\text{Me}\cdot\text{CO}_2\cdot\text{CH}_2)_2\text{O}$ , which distils at a temperature of  $204\text{—}207^{\circ}$ . In a similar manner, there have been prepared *chloromethyl propionate*, boiling at  $128\text{—}130^{\circ}$ , sp. gr. 1.140; *methylene dipropionate*, boiling at  $190\text{—}192^{\circ}$ , sp. gr. 1.503; *chloromethyl isobutyrate*, boiling at  $138\text{—}140^{\circ}$ , sp. gr. 1.080; *methylene diisobutyrate*, boiling at  $197\text{—}199^{\circ}$ , sp. gr. 0.998; *chloromethyl butyrate*, boiling at  $150^{\circ}$ , sp. gr. 1.094; *methylene dibutyrate*, boiling at  $215\text{—}216^{\circ}$ , sp. gr. 1.017; in all cases, the boiling points were determined under a pressure of 745 mm. and the sp. gr. taken at  $20^{\circ}/20^{\circ}$ .

Some of the commercial specimens of trioxymethylene are not suitable for the above reactions, but a suitable specimen can be obtained by slowly evaporating a solution of formaldehyde. A. F.

**Wood Tar of the Douglas Fir (*Pseudotsuga Taxifolia*).** By H. G. BYERS and PAUL HOPKINS (*J. Amer. Chem. Soc.*, 1902, 24, 764—771).—When the wood was distilled at temperatures below  $400^{\circ}$ , there were obtained (A) 47.5 per cent. pyroligneous acid, containing acetic acid 3.47 per cent., and methyl alcohol 4.16 per cent.; (B) 7.5 per cent. of tar containing light oil 18.0, creosote oil 23.0, pitch 39.0, and water 20.0 per cent.; (C) 30.0 per cent. of charcoal;

and (D) 15.0 per cent. of gas. At temperatures below 700°, there were obtained (A) pyroligneous acid 34 per cent., containing acetic acid 2.9, and methyl alcohol 2.9 per cent.; (B) tar 17.7 per cent., containing light oil 8.0, creosote oil 10.0, pitch 18.0, and water 64.0 per cent.; (C) charcoal 29 per cent., and (D) gases 19.3 per cent.

The gas is non-illuminating; the charcoal is soft and contains little ash.

The creosote oil boiled from 150—250° and contained 17 per cent. of creosote, of which 9.5 per cent. was guaiacol.

The light oil, which boiled between 40° and 150°, was fractionated, and contained small amounts of aldehydes and ketones and considerable amounts of the methyl and ethyl esters of formic, acetic, propionic, and butyric acids. The results of the fractionation and the yield of the products are tabulated in the original.

T. A. H.

**Behaviour of Certain Acyl Chlorides towards Agents which eliminate Hydrogen Chloride.** By EDGAR WEDEKIND (*Annalen*, 1902, 323, 246—257).—Acetyl chloride, when treated with triethylamine dissolved in benzene, loses hydrogen chloride and 4 mols. of the residue condense to form dehydracetic acid; its next homologue, propionyl chloride, behaves differently under these conditions, giving rise to a trimeric condensation product. Compounds of similar complexity have also been obtained from phenylacetyl chloride and dihydrocinnamyl chloride.

Dehydracetic acid also results from the action of ferric chloride on acetyl chloride. The homologous chlorides of the fatty series, when condensed with dry metallic chlorides, yield high-boiling oils, the constitution of which is not yet known. Benzoyl chloride and phenylacetyl chloride do not give rise to ketones under the influence of ferric chloride. The aromatic acyl chlorides containing at least three carbon atoms in the side chain condense to form cyclic ketones; dihydrocinnamyl chloride yields hydrindone, whilst phenyl-*n*-butyryl chloride and phenyl-*n*-valeryl chloride furnish  $\alpha$ -ketotetrahydronaphthalene and pheno- $\alpha$ -ketocycloheptane respectively. Cinnamyl chloride does not, however, condense to form an indenone.

Aluminium chloride also serves to promote these condensations. In ethereal solutions, the acyl chlorides, under the influence of the anhydrous metallic chlorides, give rise to the ethyl esters of the corresponding acids.

G. T. M.

**Nature of Radicles.** By EDGAR WEDEKIND (*Annalen*, 1902, 323, 257—264. Compare Vorländer, this vol., i, 309; ii, 250).—Ethyl chlorocarbonate does not form additive products with the strong tertiary bases, although it is readily decomposed by these substances, the action being accompanied by an elimination of hydrogen chloride. It follows therefore that this acyl chloride conforms to the author's rule that two negative groups, one of which is a strongly acidic radicle, do not, under ordinary conditions, form additive products with the tertiary amines. The author's study of the interaction of acyl chlorides and the tertiary bases leads to the following conclusions. The more rapid and complete is the interaction of these reagents, the

greater is the probability of an elimination of hydrogen from the molecule of the acyl chloride and the consequent formation of bye-products. On the other hand, the slower the elimination of hydrogen chloride, the greater is the tendency for the intervention of moisture, leading to the production of acid anhydrides.

*Pyridine picryl chloride*,  $C_5NH_5Cl \cdot C_6H_2(NO_2)_3$ , results from the addition of picryl chloride to pyridine; it is a yellow, amorphous powder, readily decomposed by water or the hydroxylic solvents with the production of pyridine picrate. Triethylamine appears to yield a similar product, but no addition takes place in the case of tripropylamine.  
G. T. M.

**Linseed Oil.** By S. FOKIN (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 501—503).—Contrary to the observations of some other investigators, the chief constituent of linseed oil is found to be linolic acid, together with 22—25 per cent. of linolenic acid and about 5 per cent. of solid fatty acids.

The linolic acid contained in linseed oil is apparently isomeric with those obtained from cotton-seed oil and sunflower oil. The tetrabromostearic acid prepared from linseed oil is difficult to obtain in a solid state, and then forms an amorphous mass melting at 98—101°, whilst the similar acid from other oils is distinctly crystalline and melts at 114—115°.  
T. H. P.

**Action of Organic Acids on Antimony Oxides.** By EDUARD JORDIS (*Zeit. angew. Chem.*, 1902, 15, 906—911).—The power possessed by organic acids of dissolving antimonious oxide depends entirely on the relative strength of the acids. The recent publications of Moritz and Schneider (this vol., i, 703) are criticised. K. J. P. O.

**Electrolytic Study of Pyruvic Acid.** By GEORGE W. ROCKWELL (*J. Amer. Chem. Soc.*, 1902, 24, 719—734).—When pyruvic acid, dissolved in alcohol, is oxidised electrolytically, in presence of sodium hydroxide or carbonate, or of sulphuric or hydrochloric acid, used as electrolytes, there are formed in quantities varying with the concentration, temperature, current strength, and voltage employed, acetaldehyde, ethyl acetate, carbon monoxide and dioxide, but no acetyl peroxide. When the acid is electrolytically reduced, using the same electrolytes, the amount of lactic acid produced is similarly dependent on the same factors.  
T. A. H.

**Condensation of Carbon Tetrachloride with Ethyl Malonate and Ethyl Cyanoacetate.** By OTTO DIMROTH (*Ber.*, 1902, 35, 2881—2884).—In the hope of synthesising allene derivatives ( $\cdot C:C:C \cdot$ ), carbon tetrachloride and ethyl disodiocyanacetate were caused to interact; the sodium salt of ethyl dicyanoglutaconate (Errera, Abstr., 1898, i, 297; and Ruhemann and Browning, Trans., 1897, 73, 280) was obtained and identified by conversion into the ester (m. p. 181—183°); on boiling with alcohol, the latter yielded the ammonium salt of ethyl 2:6-dihydroxypyridine-3:5-dicarboxylate (m. p. 199°). On reinvestigation of the allene derivative, ethyl allene-

tetracarboxylate, which was prepared by Zelinsky and Doroschewsky (Abstr., 1895, i, 129) by the action of ethyl disodiummalonate on carbon tetrachloride, it was found that this substance was ethyl ethoxycoumalindicarboxylate (m. p.  $94^{\circ}$ ), originally prepared by Guthzeit and Dressel (Abstr., 1889, 860) by the action of heat on ethyl dicarboxyglutaconate. Further, the first product of the action of carbon tetrachloride and ethyl disodiummalonate is not ethyl ethoxypropylenetetracarboxylate, as Zelinsky and Doroschewsky believed, but ethyl dicarboxyglutaconate (Conrad and Guthzeit, Abstr., 1884, 297).

Carbon tetrachloride and the disodio-derivatives of ethyl cyanoacetate and ethyl malonate yield the same products as chloroform and the monosodio-derivatives of these esters.

K. J. P. O.

**Isomeric Lactonic Acids Derived from  $\beta\gamma\gamma$ -Dimethyl- $\beta$ -hydroxypentanedioic Acid.** By LUIGI BALBIANO (*Gazzetta*, 1902, 32, i, 485—494).—The acid described by the author (Abstr., 1899, i, 867) as  $\gamma\gamma\delta$ -trimethylpentane- $\beta\epsilon$ -olidoic acid is now found to be a mixture of two isomerides, one  $\gamma\gamma\delta$ -trimethylpentane- $\beta\epsilon$ -olidoic acid, and the other  $\beta\gamma\gamma$ -trimethylpentane- $\beta\epsilon$ -olidoic acid, identical with the acid obtained by Blanc (Abstr., 1901, i, 119). It follows from this that the acid,  $C_8H_{12}O_5$ , obtained as the chief oxidation product of camphoric acid, does not possess the constitution  $CO_2H \cdot CO \cdot CMe_2 \cdot CHMe \cdot CO_2H$ , assigned to it by Tiemann and Mahla (Abstr., 1895, i, 678), since such an acid should give on reduction exclusively  $\gamma\gamma\delta$ -trimethylpentane- $\beta\epsilon$ -olidoic acid; as, however, this acid,  $C_8H_{12}O_5$ , when reduced gives a mixture of the two isomerides mentioned above, it must have the formula  $CMe_2 \left\langle \begin{smallmatrix} CMe(CO_2H) \\ CH(CO_2H) \end{smallmatrix} \right\rangle O$ .

$\beta\gamma\gamma$ -Trimethylpentane- $\beta\epsilon$ -olidoic acid,  $O \left\langle \begin{smallmatrix} CO-CH_2 \\ CMe(CO_2H) \end{smallmatrix} \right\rangle CMe_2$ , melts at  $165-166^{\circ}$  and crystallises in the monoclinic system [Zambonini,  $a:b:c = 0.54867:1:1.0863$ .  $\beta = 52^{\circ}5'30''$ ].

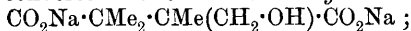
$\gamma\gamma\delta$ -Trimethylpentane- $\beta\epsilon$ -olidoic acid,  $O \left\langle \begin{smallmatrix} CO-CHMe \\ CH(CO_2H) \end{smallmatrix} \right\rangle CMe_2$ , also forms monoclinic crystals melting at  $163-164^{\circ}$  [Zambonini,  $a:b:c = 0.47994:1:1.2802$ .  $\beta = 83^{\circ}38'$ ]. The *calcium* salt crystallises with  $4H_2O$ ; the *lead* salt ( $+3H_2O$ ) separates from water in mammillary tufts of small needles melting at  $110-112^{\circ}$ , whilst in the anhydrous form it softens at  $176^{\circ}$  and melts at  $184-185^{\circ}$ .

The mixture of the two acids does not melt at  $110-120^{\circ}$  as Blanc (*loc. cit.*) stated, but at  $158-160^{\circ}$ .

T. H. P.

**Camphoric Acid. XII. Synthesis of Trimethylparaconic Acid.** By WILLIAM A. NOYES and AUSTIN M. PATTERSON (*Amer. Chem. J.*, 1902, 28, 228—232; *Ber.*, 1902, 35, 2940—2942).—Trimethylparaconic acid,  $CMe_2 \cdot CO \left\langle \begin{smallmatrix} CMe_2 \cdot CO \\ CO_2H \cdot CMe \cdot CH_2 \end{smallmatrix} \right\rangle O$ , obtained by heating a mixture of sodium trimethylsuccinate, trioxymethylene, and acetic anhydride in a sealed tube at  $120-140^{\circ}$  for two days, crystallises from hot benzene or dilute alcohol and melts and decomposes at  $256-257^{\circ}$ ; its *ethyl*

ester melts at  $34.5^{\circ}$ . When the acid is warmed with sodium hydroxide, it is converted into *sodium trimethylitamalate*,



the corresponding *silver* salt was prepared and analysed. *Diethyl trimethylitamalate* was obtained as a viscous oil; when treated with phosphorus tribromide, it is converted into ethyl trimethylparaconate

E. G.

**Anæropolarimetry.** By B. H. J. TER BRAAKE (*Rec. trav. chim.*, 1902, 21, 155—185).—The author has investigated the optical rotation of ethyl monosodium and monopotassium tartrates and of disodium and dipotassium tartrates in alcoholic solution, special precautions having been taken to avoid the absorption of water from the air. The substances are all lævorotatory, a fact which is contrary to Guye's hypothesis. The rotation of the last two compounds could not be determined exactly. The rotatory power of the monosubstituted esters increases as the concentration is increased and as the temperature is lowered. The rotatory power of the above compounds also undergoes change with time, owing to the formation of ethyl mono- and di-sodium and potassium mesotartrates and of ethyl mono- and di-sodium and potassium racemates; in the case of ethyl monosodium tartrate, the major portion is transformed into the mesotartrate.

A. F.

**Action of Water on the Ethyl Monosodium and Monopotassium Tartrates.** By B. H. J. TER BRAAKE (*Rec. trav. chim.*, 1902, 21, 186—190. Compare Mulder, *Abstr.*, 1890, 595).—By the action of water on the ethyl monosodium and monopotassium tartrates, a gelatinous precipitate separates, consisting of a mixture of ethyl sodium or potassium tartrate and of disodium or dipotassium tartrate.

A. F.

**Action of Halogen-substituted Esters of Fatty Acids on the Sodio-compounds of Saturated and Unsaturated Derivatives of Ethyl Malonate.** By MAX GUTHZEIT and MAX ENGELMANN (*J. pr. Chem.*, 1902, [ii], 66, 104—129. Compare this vol., i, 658).—*Ethyl  $\Delta^{\alpha}$ -butylene- $\alpha\gamma\delta$ -tetracarboxylate*,



prepared by the action of ethyl bromoacetate and sodium ethoxide on ethyl isoaconitate, is an oil which boils at  $216$ — $218^{\circ}$  under 14 mm. pressure, and when hydrolysed by 50 per cent. hydrochloric acid yields  *$\Delta^{\alpha}$ -butylene- $\alpha\gamma\delta$ -tricarboxylic acid*, which melts at  $148^{\circ}$ , is easily soluble in water or acetone, but sparingly so in ether, benzene, or chloroform, and gives precipitates in neutral solution with silver, lead, and copper salts. *Ethyl butane- $\alpha\beta\beta\delta$ -tetracarboxylate*, obtained by the action of ethyl bromoacetate and sodium ethoxide on ethyl carboxyglutarate (b. p.  $161^{\circ}$  under 12 mm. pressure; compare *Abstr.*, 1899, i, 261), is a colourless liquid, which boils at  $200$ — $205^{\circ}$  under 15 mm. pressure, and when hydrolysed by 10 per cent. hydrochloric acid yields  *$\alpha\beta\delta$ -butane-tricarboxylic acid*, which melts at  $118$ — $120^{\circ}$  (compare *Abstr.*, 1892, 42), is easily soluble in acetone, but sparingly so in ether or chloroform, and, when neutralised with ammonia, gives precipitates with copper, iron, silver, and lead salts.



The action of ethyl chloromalonate on ethyl sodiodicarboxylate leads to the formation of an oil, probably *ethyl*  $\Delta^{\alpha}$ -butylene- $\alpha\gamma\gamma\delta\delta$ -hexacarboxylate, which commences to decompose at  $230^{\circ}$  under 15 mm. pressure, and, on hydrolysis with dilute hydrochloric acid, yields  $\Delta^{\alpha}$ -butylene- $\alpha\gamma\delta$ -tricarboxylic acid.

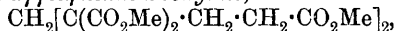
Ethyl bromoacetate reacts more easily than ethyl chloroacetate with ethyl sodiodicarboxylate, giving a better yield of ethyl butylenepentacarboxylate (this vol., i, 659), which is hydrolysed by dilute hydrochloric acid to butylenetricarboxylic acid. Ethyl butanepentacarboxylate, formed by reduction of the unsaturated ester with zinc dust in glacial acetic acid solution, boils at  $218-220^{\circ}$  under 12 mm. pressure.

The action of ethyl bromoacetate on ethyl sodiobutanepentacarboxylate in absolute alcohol leads to the formation of *ethyl* pentane- $\alpha\beta\beta\delta\delta\epsilon$ -hexacarboxylate, which crystallises from light petroleum in nacreous leaflets, melts at  $62^{\circ}$ , boils at  $230-240^{\circ}$  under 12 mm. pressure, is easily soluble in ether, chloroform, or benzene, but more sparingly so in alcohol or light petroleum, and on hydrolysis with 15 per cent. hydrochloric acid yields pentane- $\alpha\beta\delta\epsilon$ -tetracarboxylic acid (*methylene-disuccinic acid*),  $\text{CH}_2[\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}]_2$ , which forms crystalline nodules, melts and effervesces at  $214-216^{\circ}$ , is sparingly soluble in cold water or acetone, and almost insoluble in ether, benzene, or chloroform. The zinc and barium salts are precipitated only in boiling solutions and redissolve on cooling.

Ethyl pentane- $\alpha\beta\beta\delta\delta\epsilon$ -hexacarboxylate can also be obtained in a 20 per cent. yield by the action of ethyl bromoacetate on ethyl disodiodicarboxylate. There is formed in the same reaction an oil which boils at  $195-200^{\circ}$  under 12 mm. pressure, and must be ethyl propane- $\alpha\beta\beta\gamma$ -tetracarboxylate,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{C}(\text{CO}_2\text{Et})_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  (Bischoff, Abstr., 1883, 46), or ethyl propane- $\alpha\alpha\beta\gamma$ -tetracarboxylate,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CH}(\text{CO}_2\text{Et})_2$  (Emery, Abstr., 1891, 424), as on hydrolysis it yields tricarballic acid.

The action of methyl chloromalonate on methyl disodiodicarboxylate leads to the formation of methyl trimethylenetetracarboxylate (m. p.  $73^{\circ}$ ) and methyl ethanetetracarboxylate (m. p.  $137-138^{\circ}$ ).

*Methyl* heptane- $\alpha\gamma\gamma\epsilon\eta$ -hexacarboxylate,



formed by the action of methyl  $\beta$ -iodopropionate on methyl disodiodicarboxylate, melts at  $87^{\circ}$  and boils at  $170-190^{\circ}$  under 14 mm. pressure.

Ethyl dicarboxylate is more easily obtained in a pure state by the action of methylene iodide on ethyl sodiomalonate than by the action of formaldehyde on ethyl malonate in the presence of diethylamine. Ethyl pentane- $\alpha\alpha\gamma\epsilon\epsilon$ -hexacarboxylate (compare Bottomley and Perkin, Trans., 1900, 77, 294), which is formed in the later reaction, yields, with ammonia, a *hexa-amide*,  $\text{C}(\text{CO}\cdot\text{NH}_2)_2[\text{CH}_2\cdot\text{CH}(\text{CO}\cdot\text{NH}_2)]_2$ , which sinters above  $210^{\circ}$ , melts at  $230-235^{\circ}$ , and on hydrolysis with hydrochloric acid forms pentane- $\alpha\gamma\epsilon$ -tricarboxylic acid. G. Y.

**Cystein. I.** By CARL NEUBERG (*Ber.*, 1902, 35, 3161—3164. Compare Baumann, Abstr., 1882, 1).—*iso*Ethionic acid is produced when

cystein is oxidised with nitric acid of sp. gr. 1.2. This would indicate that the sulphhydryl and amino-groups are attached to different carbon atoms in the cystein molecule, which, therefore, should have the constitution  $\text{CO}_2\text{H}\cdot\text{CH}(\text{SH})\cdot\text{CH}_2\cdot\text{NH}_2$  or  $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{SH}$ .

J. J. S.

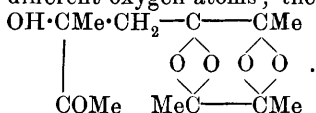
**A New Method of preparing Trithioformaldehyde.** By LUDWIG VANINO (*Ber.*, 1902, 35, 3251—3252).—When an acid is added to a solution of sodium thiosulphate containing formaldehyde, no precipitation of sulphur takes place in the cold. On warming the mixture, some sulphur is separated, and ultimately trithioformaldehyde is precipitated.

J. McC.

**Preparation of Diacetyl and a Polymerisation Product of Diacetyl.** By OTTO DIELS and HANS JOST (*Ber.*, 1902, 35, 3290—3299).—Diacetyl can be conveniently prepared from methyl ethyl ketone by treatment with amyl nitrite and boiling the *isonitroso*-ketone formed with an acid. Diacetyl, when shaken with concentrated hydrochloric acid, is converted into *termolecular diacetyl*,  $\text{C}_{12}\text{H}_{18}\text{O}_6$ , which melts at  $105^\circ$ , boils at  $280^\circ$ , and is sparingly soluble in water, but easily so in organic solvents. This polymeric diacetyl does not reduce Fehling's solution, permanganate, or silver solution. It is quite stable in presence of alkalis, but mineral acids decompose it into diacetyl, acetic acid, and other substances not yet identified. With acetic anhydride, it gives a *monoacetyl* derivative which melts at  $93^\circ$ . It forms a *phenylurethane* which crystallises from benzene with one mol. of benzene of crystallisation, melts at  $86^\circ$ , or after freeing from benzene at  $132^\circ$  (corr.). With phenylhydrazine in presence of acetic acid it gives the ordinary osazone of diacetyl. It forms a *p*-nitro-phenylhydrazone which melts at  $200^\circ$  (corr.), an *oxime* which melts at  $174$ — $175^\circ$  (corr.), and a *semicarbazone* melting at  $238^\circ$  (corr.). The acetyl derivative gives a *semicarbazone* which melts at  $206^\circ$  (corr.).

When reduced with sodium amalgam, the polymeric diacetyl yields *p*-xylcquinol and a substance which is probably dimethyl-cyclohexanone. The latter gives a *semicarbazone* melting at  $198^\circ$  (corr.).

From the behaviour of the polymeric diacetyl, it is evident that it contains a hydroxyl radicle and a ketonic group as well as four indifferent oxygen atoms; the formula provisionally suggested for it is:



J. McC.

**Action of Soluble Ferments and Top Yeast on Gentiobiose.** By ÉMILE BOURQUELOT and HENRI HERISSEY (*Compt. rend.*, 1902, 135, 399—401. Compare this vol., i, 713).—The soluble ferments of *Aspergillus* completely hydrolyse gentiobiose into 2 mols. of dextrose.

Emulsin, which hydrolyses gentiobiose, has only a slight action on gentianose, causing its solution to become more dextrorotatory. Top

yeast, on the other hand, partially hydrolyses gentianose, but does not attack gentiobiose.

Sucrose, raffinose, gentianose, and manneotetrose are all partially hydrolysed by invertin with the liberation of 1 mol. of lævulose; gentiobiose, on the contrary, is not affected by this reagent.

In order to hydrolyse gentianose completely by these ferments it is therefore necessary to treat it successively with invertin and emulsin.

G. T. M.

**Formaldehyde (Methylene) Derivatives of Sugars and Glucosides.** By CORNELIS A. LOBRY DE BRUYN and WILLIAM ALBERDA VAN EKENSTEIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 5, 175—177. Compare *Abstr.*, 1900, i, 619).—A number of mono- and di-formal derivatives can be obtained when sugars (and glucosides) are fused with trioxymethylene. Diformalxylose melts at 56—57°, has  $[\alpha]_D$  (2 per cent. solution in methyl alcohol) + 25.7°, and sublimes readily. Diformalarabinose is an oily, colourless liquid boiling at 155° under 32 mm. pressure;  $[\alpha]_D$  (2 per cent. solution in methyl alcohol) - 16°. Methylenegalactoside (mono-formal derivative) is an indistinctly crystalline substance melting at 203°;  $[\alpha]_D$  (2 per cent. aqueous solution) + 124.8°. Formalmethylene-fructoside melts at 92° and has  $[\alpha]_D$  (2 per cent. aqueous solution) - 34.9°. From *d*-sorbose, a derivative has been obtained melting at 54°, with  $[\alpha]_D$  (2 per cent. aqueous solution) - 25°; from rhamnose, a product melting at 76° and with  $[\alpha]_D$  (0.4 per cent. aqueous solution) - 18°; mannose also yields a crystalline derivative.

Crystalline formal derivatives were obtained from methylmannoside (m. p. 127°;  $[\alpha]_D$  + 10.5), from  $\beta$ -methyl-*d*-glucoside (m. p. 136°, inactive), and from  $\alpha$ - and  $\beta$ -methyl-*d*-galactosides. The derivatives obtained from  $\alpha$ -methyl-*d*-glucoside and amyl- and ethyl-*d*-glucosides are viscous liquids.

J. C. P.

**Preparation of Osones from Osazones derived from Sugars.** By EMIL FISCHER and E. FRANKLAND ARMSTRONG (*Ber.*, 1902, 35, 3141—3144).—Herzfeld (*Ber.*, 1895, 28, 442) has shown that benzaldehyde may replace hydrochloric acid in the decomposition of phenylhydrazones. A similar method cannot be adopted in the case of the phenylosazones of the monosaccharides, since, in most cases, they are not sufficiently soluble in water. The phenylosazones of disaccharides, however, are completely decomposed when their aqueous solutions are boiled for a short time with benzaldehyde, and good yields of the osones are obtained. The method is also applicable to the osazones of arabinose and xylose, which are soluble in hot water.

Maltosone has been obtained in the form of a syrup which sets to a vitreous, amorphous mass. It reduces Fehling's solution, and reacts with phenylhydrazine yielding maltosazone; with *p*-bromophenylhydrazine it yields *p*-bromophenylmaltosazone, which crystallises in yellow needles melting and decomposing at 198° and only sparingly soluble in the ordinary solvents with the exception of hot alcohol. Yeast enzymes hydrolyse maltosone to glucosone.

*Melibiosone* in aqueous solution has a low dextrorotation, and is

hydrolysed by emulsin. *p*-Bromophenylmelibiosazone crystallises in yellow needles melting at 182°. J. J. S.

**Synthesis of New Disaccharides.** By EMIL FISCHER and E. FRANKLAND ARMSTRONG (*Ber.*, 1902, 35, 3144—3153. Compare E. Fischer, *Abstr.*, 1891, 413).—Three new disaccharides have been obtained by the action of tetra-acetylchlorodextrose on the sodium derivative of galactose and by the action of tetra-acetylchlorogalactose on the sodium derivatives of dextrose and galactose. It is probable that these compounds are similarly constituted to the glucosides, and they are respectively named *glucosidogalactose*, *galactosidodextrose*, and *galactosidogalactose*. They yield phenylosazones which are relatively readily soluble in water. Top yeasts do not ferment the three disaccharides, and they may be freed from monosaccharides by the action of these yeasts. Bottom yeasts decompose glucosidogalactose and galactosidoglucose, but not galactosidogalactose. All three disaccharides are hydrolysed by emulsin after contact for several days at 35°, but not by kephir lactase. Galactosidoglucose is probably identical with melibiose; its phenylosazone melts at 173—174° and the *p*-bromophenylosazone at 181°, both a few degrees lower than the corresponding compounds from melibiose.

*Phenylglucosidogalactosazone* melts at 175—177° (corr.); it is somewhat less soluble in benzene or toluene than galactosidoglucosazone.

*Phenylgalactosidogalactosazone* melts at 176—178° (corr.), is only sparingly soluble in chloroform, benzene, or toluene, and insoluble in ether or light petroleum. All three osazones yield osones when their aqueous solutions are boiled with benzaldehyde.

Kephir lactase partially converts solutions of pure galactose into a new disaccharide, *isolactose*, the *osazone* of which crystallises in yellow needles melting at 193—196° (corr.). The sugar is not fermented by top, but is by bottom, yeasts, and is also hydrolysed by kephir lactase.

J. J. S.

**Isomeric Acetohalogen Derivatives of Sugars and Synthesis of Glucosides.** III. By EMIL FISCHER and E. FRANKLAND ARMSTRONG (*Ber.*, 1902, 35, 3153—3155. Compare *Abstr.*, 1901, i, 257, 671, and this vol., i, 263).— $\beta$ -Hepta-acetylbromomaltose,  $C_{26}H_{35}O_{17}Br$ , obtained by the action of dry liquid hydrogen bromide on octa-acetylmaltose in sealed tubes at the ordinary temperature, crystallises from light petroleum in colourless prisms melting at 84° (corr.). It reacts with sodium phenoxide, yielding hepta-acetylphenylmaltoside,  $C_{32}H_{40}O_{18}$ , which melts at 157—158° (corr.) and is only sparingly soluble in hot water or dilute acids. On hydrolysis with barium hydroxide, it yields  $\beta$ -phenylmaltoside,  $C_{12}H_{21}O_{10} \cdot OPh$ , in the form of small, colourless prisms melting at 96° and with  $[\alpha]_D + 34.0^\circ$  at 20°. Tetra-acetylethylgalactoside may be readily obtained by the action of ethyl alcohol on  $\beta$ -tetra-acetylchlorogalactose in the presence of silver carbonate; it melts at 88° (corr.) and has  $[\alpha]_D - 29.8^\circ$  at 20°; on hydrolysis with barium hydroxide, it yields  $\beta$ -ethylgalactoside melting at 153—155° and with  $[\alpha]_D - 4.0^\circ$  at 20°.

$\beta$ -Methyl-,  $\beta$ -ethyl-, and  $\beta$ -phenyl-galactosides are hydrolysed by emulsin and also by kephir extract.

J. J. S.

**Optical Rotatory Power of Sucrose when dissolved in Amines.** By GUY MAURICE WILCOX (*J. Physical Chem.*, 1902, 6, 339—342).—It was found that rotation of sugar in solutions in allylamine, amylamine, and isopropylamine is considerably greater than in water. In amylamine and allylamine solution, the rotation was found to decrease with increasing concentration; in the case of isopropylamine solution, only one observation was made, so that the effect of concentration was not determined.

L. M. J.

**Isomerism of the  $\beta$ -Naphthylhydrazones of the Sugars.** By WILLIAM ALBERDA VAN EKENSTEIN and CORNELIS A. LOBRY DE BRUYN (*Ber.*, 1902, 35, 3082—3085. Compare Abstr., 1896, i, 588; 1897, i, 41).—The results recently obtained by Hilger and Rothenfusser (this vol., ii, 479) on the  $\beta$ -naphthylhydrazones of some sugars do not agree with the former observations of the authors (*loc. cit.*). This difference is due to the formation of stereoisomeric compounds. The *galactose- $\beta$ -naphthylhydrazone* obtained by the authors melts at 167° and has  $[\alpha] + 24^\circ$ , whilst that obtained by Hilger and Rothenfusser has  $[\alpha] + 10^\circ$ . *Dextrose- $\beta$ -naphthylhydrazone* has been obtained as a very soluble substance melting at 95° with  $[\alpha]_{\text{Auer}} + 40^\circ$ ; as a substance melting at 125°, and with lower rotatory power, and in a third form melting at 158—159° and having  $[\alpha]_{\text{Auer}} + 22^\circ$ .

From levulose, two isomeric  $\beta$ -naphthylhydrazones can be obtained according to the conditions.

J. McC.

**Synthesis of Carbohydrates and the Explanation of Natural Processes based thereon.** By JULIUS WALTHER (*Chem. Zeit.*, 1902, 26, 763—771. Compare this vol., ii, 203).—The author has confirmed his former observations (*loc. cit.*) and discusses their bearing on the physiological processes of plants and animals.

K. J. P. O.

**Reaction between Benzene and Cellulose. II.** By A. M. NASTUKOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 505—508. Compare this vol., i, 362).—The compound obtained by the action of benzene on a sulphuric acid solution of cellulose, which the author previously thought to be tetraphenylcellulose (*loc. cit.*), is now found to contain sulphur. The composition of the product when dried at the ordinary temperature in the desiccator is  $\text{C}_{180}\text{H}_{134}\text{O}_{25}\text{S}_2$ , whilst when dried at 105—110° it has the formula  $\text{C}_{180}\text{H}_{128}\text{O}_{22}\text{S}_2$ ; these formulæ correspond with 6 mols. of tetraphenylcellulose +  $2\text{SO}_2$ , less 9 and  $12\text{H}_2\text{O}$  respectively. The main product obtained on dry distillation of this compound is toluene, whilst when oxidised with potassium permanganate it yields benzoic acid; hence the phenyl groups present must be directly connected with carbon atoms.

T. H. P.

**Crystalline Forms of Platinichlorides of the Aliphatic Amines.** By A. RIES (*Zeit. Kryst. Min.*, 1902, 36, 321—385).—Detailed crystallographic descriptions are given of the platinichlorides of the primary, secondary, and tertiary fatty amines and quaternary ammonium compounds, and of a few of the corresponding compounds

containing bromine, iridium, or tin. The results are compared and discussed, especially with respect to their morphotropic relations.

L. J. S.

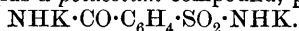
**Action of Formaldehyde on Creatine and Creatinine.** By MAX JAFFÉ (*Ber.*, 1902, 35, 2896—2901).—On treating a cold aqueous solution of creatine with dilute formaldehyde, no reaction takes place, but on heating, a *substance*,  $C_6H_{11}O_3N_3 \cdot 2H_2O$ , separates in very long, colourless needles, which lose water at  $100-105^\circ$ , decompose at  $250^\circ$ , and are fairly soluble in water and other solvents; it does not react with the usual formaldehyde reagents. On benzoylating by the Schotten-Baumann method, a *dibenzoyl* derivative,  $C_6H_9O_3N_3Bz_2$ , is obtained as colourless needles melting at  $265-266^\circ$ . Creatinine yields the same substance on treatment with formaldehyde. It probably has the formula  $OH \cdot CH_2 \cdot N : C \begin{smallmatrix} N(CH_2 \cdot OH) \\ NMe-CH_2 \end{smallmatrix} > CO$ .

K. J. P. O.

**Reactions between Acid and Basic Amides in Liquid Ammonia.** By EDWARD C. FRANKLIN and ORIN F. STAFFORD (*Amer. Chem. J.*, 1902, 28, 83—107).—Franklin and Kraus (*Abstr.*, 1900, ii, 382) have shown that a close analogy exists between liquid ammonia and water as electrolytic solvents, and that acid and basic amides bear a relation to liquid ammonia similar in many respects to that of ordinary acids and bases to water. From these considerations, it seemed probable that reaction would take place between an acid and a basic amide in liquid ammonia with the facility which marks the interaction of ordinary acids and bases in water. This has been found to be the case by means of a large number of experiments carried out in a specially devised apparatus.

Potassamide is very soluble in liquid ammonia and separates from concentrated solutions as a colourless, well crystallised, hygroscopic mass. When potassamide (1 mol.) and acetamide (1 mol.) are allowed to react in presence of liquid ammonia, hydrogen is evolved and crystals of *potassiumacetamide*,  $CH_3 \cdot CO \cdot NHK, nNH_3$ , separate from the solution; this substance is also formed by the action of potassium on a solution of acetamide in liquid ammonia. When left in the air, the crystals lose their ammonia of crystallisation and become opaque. By the action of potassium amide (2 mols.) on acetamide (1 mol.), a *dipotassiumacetamide*,  $CH_3 \cdot CO \cdot NK_2$ , is produced.

The *mono-* and *di-potassium* derivatives of benzamide, benzenesulphonamide, *m*-methoxybenzenesulphonamide, *p*-methoxybenzenesulphonamide, sulphamide, and carbamide, and the *mono-potassium* derivatives of phenylacetamide and *p*-toluenesulphonamide were also prepared. Benzoicsulphinide yields a *potassium* compound, probably



The reactions between potassamide and formamide, dichloroacetamide, thioacetamide, cyanoacetamide, *p*-chlorobenzamide, succinimide, thiocarbamide, allylthiocarbamide, picramide, and *m*-nitro-*p*-toluidine were also studied, but although in each case action evidently occurred, the products could not be isolated.

When sodamide (1 mol.) is brought in contact with acetamide (1 mol.) in solution in liquid ammonia, *sodiumacetamide*,



is produced; this compound is also formed by the action of sodium on a solution of acetamide.

Magnesium was found to react with acetamide, benzenesulphonamide, benzoicsulphinide, benzamide, phenylacetamide, cyanoacetamide, and cyanamide, whilst formamide, toluenesulphonamide, succinamide, and sulphamide were without appreciable action. *Magnesium-acetamide*, *-benzenesulphonamide*, and *-cyanamide* were prepared and analysed.

Magnesium, sodium, and potassium readily react with solutions of ammonium salts; when magnesium is treated with solution of ammonium nitrate or bromide, magnesium nitrate or bromide separates from the solution.

E. G.

#### Action of Mercuric Bromide on the Alkali Thiocyanates.

By HERMANN GROSSMAN (*Ber.*, 1902, 35, 2945—2946).—Mercuric bromide dissolves in solutions of the alkali thiocyanates forming two series of salts. One series contains one mol. of each constituent, the *ammonium* salt,  $\text{HgBr}_2\cdot\text{NH}_4\text{SCN}$ , which crystallises in stable needles, being described. The other series contains two mols. of the thiocyanate to one mol. of mercuric bromide. The *ammonium* salt,



of this series is deliquescent, but the *potassium* salt,  $\text{HgBr}_2\cdot 2\text{KSCN}$ , is crystalline and stable in air.

R. H. P.

**Action of Ethyl Iodide on Potassium Stannite.** By PAUL PFEIFFER (*Ber.*, 1902, 35, 3303—3307).—When a strong alkaline solution of stannous hydroxide is boiled with ethyl iodide and alcohol, the resulting solution deposits tin diethyl oxide. The formation of this compound is probably due to the action of the alkali on the potassium ethylstannite at first formed according to the equation  $2\text{SnEtO}\cdot\text{OK} = \text{SnEt}_2\text{O} + \text{SnO}_3\text{K}_2$ .

R. H. P.

#### Genesis of Naphthenes and Naphthenecarboxylic Acids.

By OSSIAN ASCHAN (*Annalen*, 1902, 324, 1—39).—The author's experimental results support the theory which assumes that the naphthenes and their carboxylic acids are secondary products of the distillation of mineral oil in the earth's interior, being formed by the polymerisation of compounds of the olefine series which result from the initial decomposition of fossil fat.

Although ethylene, when dissolved in carbon disulphide and treated with anhydrous aluminium chloride, does not, at the ordinary temperature, undergo any polymerisation, yet, under these conditions, the crude amylene derived from amyl alcohol gives rise to saturated hydrocarbons. The products of lowest boiling point contained in the fractions 32—35° and 35—40° consist chiefly of a saturated hydrocarbon,  $\text{C}_5\text{H}_{10}$ , closely resembling methylcyclobutane.

The next fraction, 56—62°, contains a hexane,  $\text{C}_6\text{H}_{14}$ , which corresponds in boiling point with  $\beta\gamma$ -dimethylbutane or  $\beta$ -methylpentane. The addition of a methyl group to the amylene carbon chain by the action of aluminium chloride has hitherto not been observed.

The fraction 76—81° contains a saturated hydrocarbon,  $C_6H_{12}$ , corresponding in composition with *cyclohexane*.

The fraction 150—200° appears to consist of a mixture of paraffins,  $C_{10}H_{22}$ ,  $C_{11}H_{24}$ , and  $C_{12}H_{26}$ .

When pure amylene (b. p. 37—39°) is employed in these experiments, the fraction 55—60° probably contains a branched chain hexane, whilst the fraction 260—265° consists chiefly of naphthenes mixed with small quantities of the paraffins  $C_{15}H_{32}$ .

The tarry residues of these fractionations, when distilled under diminished pressure, yield a hydrocarbon,  $C_{38}H_{66}$ , boiling at 190—220° under 30 mm. pressure.

In one series of experiments, *cyclohexane*, when heated with fuming hydriodic acid at 300°, became converted into methyl*cyclopentane*.

A negative result was obtained in a second series of experiments. *cyclohexane* also undergoes transformation when left in contact with anhydrous aluminium chloride.

It was not found possible to oxidise methyl*cyclopentane* to a cyclic monocarboxylic acid; dibasic acids only were obtained, namely, succinic, adipic, and a trace of glutaric acid. In one case, *αα*-dimethylpropionic and *isovaleric* acids were identified, these products being probably due to the oxidation of the paraffins present in the methyl*cyclopentane*.

When treated with dilute nitric acid, the cyclic hydrocarbon becomes oxidised to a mixture of acetic and succinic acids.

G. T. M.

**Methylcyclohexenes and Methylcyclohexenones.** By OTTO WALLACH (*Ber.*, 1902, 35, 2822—2825) —Cyclic alcohols, when dehydrated with phosphoric oxide or zinc chloride, often form unsaturated ring hydrocarbons, which are isomerides of those which would be expected from the constitution of the alcohol. These isomerides form less soluble nitrosyl chlorides and nitrosates than the untransformed hydrocarbons.

The *tetrahydrotoluene*, obtained when 1-methylcyclohexan-3-ol is dehydrated by zinc chloride, differs from that previously described (*Abstr.*, 1896, i, 310). It boils at 106—107°, has a sp. gr. 0.799,  $n_D$  1.44234 at 20°, and  $n_D$  +17°45' in a 1 dm. tube. The nitrosate reacts with piperidine forming the *nitrolepiperidide*, which is a beautifully crystalline compound melting at 152—153°. When the nitrosate is warmed with alcoholic potash, a liquid methylcyclohexenoneoxime,  $C_7H_{10}NOH$ , is obtained, which, when hydrolysed with sulphuric acid, yields a methylcyclohexenone,  $C_7H_{10}O$ . This ketone boils at 179—181°, is soluble in water, has a sp. gr. 0.97, and  $n_D$  1.4843 at 21°, forms a semicarbazone which melts at 207—208°, and therefore differs from the methylcyclohexenone described by Knoevenagel (*Abstr.*, 1897, i, 606). The exact constitution of these compounds has not been determined.

R. H. P.

**Action of Sulphur Chloride on Benzene.** By EDUARD LIPPMANN and ISIDOR POLLAK (*Monatsh.*, 1902, 23, 669).—If commercial benzene is warmed on a water-bath with 15 per cent. of sulphur



chloride until the evolution of hydrogen chloride ceases (192 hours), and is then washed with dilute sodium hydroxide solution, and dried over calcium chloride, it distils at  $81^{\circ}$  and is free from thiophen. G. Y.

**Organic Additive Compounds.** By PAUL LEMOULT (*Compt. rend.*, 1902, 135, 346—348).—1-Chloro-2:4-dinitrobenzene combines with tertiary bases of the diphenylmethane series to form coloured additive products.

The compounds  $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2, \text{CH}_2(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$  and  $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2, \text{CH}_2(\text{C}_6\text{H}_4 \cdot \text{NEt}_2)_2$  and crystallise in reddish-brown needles and melt at  $72^{\circ}$  and  $42.5^{\circ}$  respectively. 1-Chloro-2:4:6-trinitrobenzene and 4:4'-tetramethyldiaminodiphenylmethane give rise to the compound

$\text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)_3, \text{CH}_2(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , which separates in black flakes and melts at  $71^{\circ}$ . The 2:4-dinitrophenoxide,  $\text{OH} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2, \text{CH}_2(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , separates in large, black crystals melting at  $72^{\circ}$ ; the *picrates*,  $\text{OH} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_3, \text{CH}_2(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$  and  $\text{OH} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_3, \text{CH}_2(\text{C}_6\text{H}_4 \cdot \text{NEt}_2)_2$ , crystallise in yellow leaflets and melt respectively at  $185^{\circ}$  and  $190^{\circ}$ . Picramide gives rise to the compound  $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2)_3, \text{CH}_2(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , crystallising in lustrous, black leaflets and melting at  $106^{\circ}$ .

These substances are all readily dissociated into their generators even in their solutions in the organic solvents. G. T. M.

**Nitroethylbenzene and its Tetrazo-dye.** By GUSTAV SCHULTZ and J. FLACHSLÄNDER (*J. pr. Chem.*, 1902, [ii], 66, 153—172. Compare Abstr., 1884, 902, and Beilstein and Kuhlberg, *Annalen*, 1870, 156, 206).—*o*-Nitroethylbenzene melts at  $-23^{\circ}$  and boils at  $223-224^{\circ}$ . *p*-Nitroethylbenzene melts at  $-32^{\circ}$ , boils at  $241-242^{\circ}$ , and forms a sodium sulphonate,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Et} \cdot \text{SO}_3\text{Na} \cdot 2\text{H}_2\text{O}$ , which crystallises in long needles and is easily soluble in water.

Diaminodiethyldiphenyl, prepared from *o*-nitroethylbenzene (Schultz, *loc. cit.*), forms a dihydrochloride,  $\text{C}_{16}\text{H}_{20}\text{N}_2 \cdot 2\text{HCl}$ , which crystallises in mother-of-pearl leaflets and is easily soluble in water or hot alcohol, and a dibenzylidene derivative,  $\text{C}_{16}\text{H}_{16}\text{N}_2(\text{CHPh})_2$ , which crystallises from alcohol in yellow needles, melts at  $124-125^{\circ}$ , is easily soluble in hot alcohol, more sparingly so in cold alcohol or ether, and is hydrolysed by dilute mineral acids. The *dipicrate*, formed in alcoholic solution in presence of excess of picric acid, crystallises in glistening, golden leaflets, decomposes without melting at  $225^{\circ}$ , and on recrystallisation from alcohol is hydrolysed to the *monopicrate*, which separates in glistening, yellow needles, decomposes at  $225-230^{\circ}$ , and is only sparingly soluble in water or alcohol.

Benzidine forms a *dipicrate* which decomposes at  $190^{\circ}$ , is sparingly soluble in ether, but easily so in water or alcohol; it is stable in absolute alcohol, but is completely hydrolysed to benzidine and picric acid on recrystallisation from aqueous alcohol, and more slowly on contact with aqueous alcohol in the cold. *Tolidine dipicrate* decomposes at  $215^{\circ}$ , is stable in absolute alcohol, and on recrystallisation from aqueous alcohol is hydrolysed, but more slowly than the benzidine salt. When left with aqueous alcohol in the cold, tolidine dipicrate

is only partly hydrolysed, probably to the monopicate. The mother liquor from the preparation of 4:4'-diamino-3:3'-diethyldiphenyl contains *o*-aminoethylbenzene and a *base* which is obtained as a thick syrup soluble in alcohol or ether, and may be 4-amino-3:2'-diethyldiphenylamine or, less probably, 2:4'-diamino-3:3'-diethyldiphenyl. It forms a *hydrochloride*,  $C_{16}H_{20}N_2 \cdot 2HCl$ , which crystallises in leaflets from alcohol, in which it is sparingly soluble, a *benzylidene* derivative,  $C_{16}H_{18}N_2 \cdot CHPh$ , which crystallises in glistening leaflets, melts at  $110-112^\circ$ , and is soluble in alcohol or benzene, and a *picrate*,  $C_{16}H_{20}N_2 \cdot C_6H_3O_7N_3$ , which crystallises from alcohol in golden-yellow leaflets, decomposes at  $235-240^\circ$ , and is only sparingly soluble in water or alcohol. With ferric chloride in dilute hydrochloric acid solution, the base gives a blue-green coloration, which disappears on addition of concentrated hydrochloric acid.

When diazotised with 2 mols. of sodium nitrite and coupled with  $\alpha$ -naphthylamine-4-sulphonic acid, benzidine, *o*-tolidine, and diamino-diethyldiphenyl yield similar dyes (sodium salts). The reaction takes place most easily with benzidine, least easily with diaminodiethyldiphenyl. The new dye forms green, glistening crystals and is less soluble in water and more stable towards light and acetic acid than the dye derived from *o*-tolidine, which is also less soluble and more stable than the benzidine dye.

Of the dyes (sodium salts) obtained by coupling with  $\beta$ -naphthylamine-6-sulphonic acid, that derived from benzidine is insoluble in water, those from *o*-tolidine and diaminodiethyldiphenyl are soluble. Dyes have also been obtained by coupling diazotised diaminodiethyldiphenyl with salicylic acid and with 8-amino- $\alpha$ -naphthol-3:6-sulphonic acid.

G. Y.

**Study of Bisnitrosylbenzyl and the Bye-products obtained in its Formation.** By WILHELM BEHRENS and ROBERT BEHREND (*Annalen*, 1902, **323**, 265—278. Compare Bamberger and Renauld, *Abstr.*, 1898, i, 20; Bamberger and Szolayski, *Abstr.*, 1901, i, 84).—The compound obtained as a bye-product in the preparation of bis-nitrosylbenzyl by oxidising  $\beta$ -benzylhydroxylamine with chromic acid is benzaldoxime anhydride,  $(C_6H_5 \cdot CH \cdot N)_2O$ , corresponding in its properties with the substance produced by the aerial oxidation of the same hydroxylamine derivative. In the former reaction, the anhydride is accompanied by an oily mixture of benzaldehyde, benzyl benzoate, and benzonitrile (?).

Bisnitrosylbenzyl, when dissolved in chloroform and treated with hydrogen chloride, undergoes a complicated change, giving rise to benzoylhydrazine, benzoylbenzylidenhydrazine, hydrazine, benzyl chloride, benzaldehyde, tarry products, and probably a trace of benzonitrile.

Bisnitrosylbenzyl is scarcely attacked by bromine in hot chloroform solution and is not affected by permanganate solution; with nitric acid, it yields a mixture of nitrobenzoic acids.

G. T. M.

**Electrolytic Oxidation of Naphthalene.** By A. PANCHAUD DE BOTTENS (*Zeit. Elektrochem.*, 1902, **8**, 673—675).—When a cold

solution of naphthalene in a mixture of acetone and sulphuric acid is electrolysed, some  $\alpha$ -naphthaquinone is formed at the anode and a considerable quantity of a brown, non-crystalline substance. Naphthalene- $\alpha$ -sulphonic acid or its sodium salt and 1-amino- $\beta$ -naphthol-4-sulphonic acid, dissolved in water or a mixture of acetone and sulphuric acid, gave small quantities of phthalic acid. T. E.

**Halogen-substituted Dinitronaphthalenes.** By FRITZ ULLMANN and FORTUNATO CONSONNO (*Ber.*, 1902, 35, 2802—2811).—5-Bromo- $\alpha$ -naphthylamine, obtained by reducing Guareschi's 5-bromo- $\alpha$ -nitronaphthalene with stannous chloride, melts at 69° and yields an *acetyl* derivative crystallising in pale pink, twinned needles and melting at 215°.

5-Bromo-1 : 8-dinitronaphthalene is produced by nitrating 5-bromo- $\alpha$ -nitronaphthalene or  $\alpha$ -bromonaphthalene; when heated with alcoholic ammonia, it yields 4 : 5-dinitro- $\alpha$ -naphthylamine, which separates from glacial acetic acid in reddish-brown crystals melting at 243°. 4 : 5-Dinitro- $\alpha$ -naphthylmethylaniline is produced in a similar manner by the use of methylaniline; it forms brick-red crystals and decomposes at 259°. 4 : 5-Dinitro- $\alpha$ -naphthyl-dimethylaniline, prepared by the interaction of 5-bromo-1 : 8-dinitronaphthalene and dimethylaniline, crystallises in dark red needles and melts at 176°.

4 : 5-Dinitro- $\alpha$ -naphthol, resulting from the action of sodium carbonate solution under pressure on the bromonitro-compound, decomposes at 208°. Friedländer gives the decomposition temperature as 230° (compare *Abstr.*, 1900, i, 150).

4 : 5-Dinitronaphthyl methyl ether, produced by heating 5-bromo-1 : 8-dinitronaphthalene with an alcoholic solution of sodium methoxide, separates from ether in yellow, feathery crystals melting at 216°.

4 : 5-Dinitronaphthyl ethyl ether crystallises in nacreous leaflets and melts at 182° (compare Heermann, *Abstr.*, 1891, 1379.)

8-Chloro- $\alpha$ -nitronaphthalene, the product of the action of chlorine on  $\alpha$ -nitronaphthalene in the presence of ferric chloride, on reduction, yields 8-chloro- $\alpha$ -naphthylamine which melts at 89° and gives an *acetyl* derivative crystallising in colourless needles and melting at 137°.

4-Chloro-1 : 5-dinitronaphthalene, melting at 138°, results from the nitration of the preceding nitro-compound; it yields 4 : 8-dinitro- $\alpha$ -naphthylamine when heated with alcoholic ammonia, this product crystallising in brick-red needles and decomposing at 197°.

4 : 8-Dinitro- $\alpha$ -naphthol, produced from the corresponding bromo-dinitro-compound by the action of sodium carbonate solution at 135°, melts at 235°, not at 135° as formerly stated. G. T. M.

**Constitution of Primary Dinitrohydrocarbons.** By ROLAND SCHOLL (*J. pr. Chem.*, 1902, [ii], 66, 206—207. Compare Ponzio, this vol., i, 334).—The author draws attention to his observations on the reduction of diphenyldinitromethane (*Abstr.*, 1891, 315). Ponzio's suggestion that, in the fatty dinitro-compounds, only one nitrogen atom is attached to carbon, has been made before but can no longer be maintained (compare *Abstr.*, 1896, i, 198 ; 1901, i, 495). G. Y.

**Tervalent Carbon. IV.** By MOSES GOMBERG (*J. Amer. Chem. Soc.*, 1902, 24, 597—628. Compare Abstr., 1901, i, 78).—When a solution of iodine is added to triphenylmethyl or one of its additive products, dissolved in an appropriate solvent, 80 per cent. of the theoretical yield of triphenyliodomethane is formed (*loc. cit.*). When the solvent is petroleum, the substance separates in yellow prisms which melt at 131—132° and are soluble in benzene, carbon disulphide and hot ethyl acetate, but insoluble in ether. It reacts like the corresponding bromo- and chloro-derivatives when treated with water, alcohol, and metals, and like them forms coloured additive compounds with the chlorides of tin, zinc, and antimony. With ammonia and amines, triphenyliodomethane also reacts in the usual manner, furnishing with ammonia, triphenylaminomethane; with ethylamine, triphenylmethylaminomethane; and with aniline, toluidine, &c., similar derivatives.

When the amount of iodine calculated for the formula  $\text{CPh}_3\text{I}_5$  is added to a solution of triphenyliodomethane prepared as already described, there separates a penta-iodide of the above formula as dark blue, lustrous needles which melt at 90°. With sodium thiosulphate, only the "external" iodine is attacked with the formation of triphenyliodomethane and ultimately triphenylcarbinol. Alcohol converts the penta-iodide into triphenylmethane, but if the hydrogen iodide first formed be removed by addition of zinc dust, triphenylcarbinyl ethyl ether is obtained. Zinc dust, when added to neutral solutions of the periodide, furnishes triphenylmethyl.

Triphenylbromomethane penta-iodide,  $\text{CPh}_3\text{BrI}_5$  (compare Abstr., 1899, i, 155), prepared by addition of the calculated quantity of iodine to solutions of triphenylbromomethane, separates as an oil which becomes crystalline in a few seconds. It is slightly soluble in benzene or carbon disulphide, but readily so in ether. Its reactions are similar to those of the preceding compound.

The author points out that the results recorded in this and previous papers are all in favour of the view that the hydrocarbon which he has named triphenylmethyl has the constitution  $\text{CPh}_3$  in which carbon is tervalent.

T. A. H.

**Dibenzylanthracene.** By EDUARD LIPPMANN and ISIDOR POLLAK (*Monatsh.*, 1902, 23, 672—679).—5:10-Dibenzylanthracene, prepared by heating anthracene with benzyl chloride and zinc dust in carbon disulphide solution, crystallises from benzene in glistening, whitish-yellow needles, melts at 239—240°, has a sp. gr. 0.1787 at 16°, and is only sparingly soluble in benzene, ether, carbon disulphide, or glacial acetic acid, and insoluble in alcohol or light petroleum. On oxidation with chromic acid in glacial acetic acid solution, it gives an almost quantitative yield of anthraquinone melting at 273°. On bromination in carbon disulphide solution, dibenzylanthracene yields a bromo-derivative,  $\text{CH}_2\text{Ph}\cdot\text{C}_{14}\text{H}_8\cdot\text{CHBrPh}$ , which crystallises in glistening, yellow leaflets, commences to lose hydrogen bromide at 160°, and melts at 187°. It is easily soluble in benzene or carbon disulphide, but only sparingly so in alcohol or ether. When boiled with water containing potassium carbonate or with glacial acetic acid, it is converted into hydroxydibenzylanthracene,  $\text{CH}_2\text{Ph}\cdot\text{C}_{14}\text{H}_8\cdot\text{CHPh}\cdot\text{OH}$ , which forms

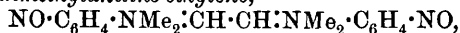
yellow crystals, melts at 225—226°, and is easily soluble in ether, benzene, or carbon disulphide, but only sparingly so in alcohol. The *ethyl* ether crystallises in soft leaflets, melts at 218°, and forms a fluorescent solution in benzene. G. Y.

**Hexaphenylethane.** By FRITZ ULLMANN and W. BORSUM (*Ber.*, 1902, 35, 2877—2881).—On attempting to prepare triphenylmethane by the reduction of triphenylmethyl chloride with zinc in acetic acid solution, *hexaphenylethane*,  $\text{CPh}_3 \cdot \text{CPh}_3$ , was formed when the reduction was carried out with zinc and stannous chloride in acetic acid solution in the presence of hydrochloric acid, the yield amounted to 60—70 per cent. The hydrocarbon can be also obtained by reducing triphenylcarbinol in a similar manner. It forms small, colourless crystals, soluble in benzene or toluene, which melt at 231° (corr.), and boil at a higher temperature than sulphur. It is oxidised by chromic acid only with great difficulty, yielding triphenylcarbinol; by nitric acid, it is converted into a hexanitro-derivative, which melts at 265°. When the reduction of triphenylmethyl chloride is carried out in the complete absence of water, only the triphenylmethyl peroxide (m. p. 185°) prepared by Gomberg (*Abstr.*, 1901, i, 77) is obtained.

K. J. P. O.

**Action of Ethylene Dibromide on *p*-Nitrosodimethylaniline.** By HENRY A. TORREY (*Amer. Chem. J.*, 1902, 28, 107—121).—When *p*-nitrosodimethylaniline is heated with an excess of ethylene dibromide, di-*p*-nitrosodimethylaniline-ethylene and *p*-nitrosodimethylaniline hydrobromide are produced.

*Di-p-nitrosodimethylaniline-ethylene*,



crystallises from amyl alcohol in deep red needles, decomposes at 230—240°, and is soluble in chloroform or glacial acetic acid; the *picrate* melts and decomposes at about 155°. If *p*-nitrosodimethylaniline is heated with an alcoholic solution of ethylene dibromide, the red ethylene derivative first formed suffers decomposition with production of tetramethyldiaminoazobenzene; the same compound is obtained when the red ethylene derivative itself is heated with *p*-nitrosodimethylaniline and alcohol. When the ethylene derivative is treated with dilute nitric acid, decomposition occurs with formation of formic acid, *p*-nitrosodimethylaniline *nitrate*, which melts and decomposes at 162°, and a *substance* which crystallises in yellow plates, melts at 255—256°, and does not contain oxygen.

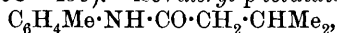
*p*-Nitrosodimethylaniline *hydrobromide* forms yellow crystals and decomposes at 207°. The *platinichloride* obtained by the action of platinic chloride on an alcoholic solution of the hydrochloride differs from the two platinum salts described by Schraube (*Ber.*, 1875, 8, 616). The *picrate* decomposes at about 140°.

E. G.

**Influence of the Solvent on the Orientation of the Isomerides obtained on Nitration in the Aromatic Series.** By CARL SCHWALBE (*Ber.*, 1902, 35, 3301—3303).—A preliminary note on the influence of the solvent during the nitration of ring compounds. Benzylideneaniline, when nitrated in concentrated sulphuric acid solution with nitric acid at 5°, yields *p*-nitroaniline only, but in glacial

acetic acid solution with nitric acid and acetic anhydride gives rise to a mixture of *p*- and *o*-nitroaniline (see Pictet and Genequand, this vol., i, 584). R. H. P.

*iso*Valeryl *p*-toluidide and *m*-Bromo*iso*valeryl *p*-toluidide. By FRANCESCO MAFFEZZOLI (*Chem. Centr.*, 1902, ii, 504—505; from *Boll. Chim. Farm.*, 41, 458—459).—*iso*Valeryl *p*-toluidide,



prepared by the action of phosphorus trichloride on a mixture of *p*-toluidine and *isovaleric* acid, crystallises from a large volume of boiling water in colourless, monoclinic plates, has a slight odour of valeric acid, melts at 98°, and is very readily soluble in alcohol, ether, chloroform, or benzene, but only slightly so in cold water. The *m*-bromo-derivative forms small, colourless, needle-shaped crystals, is odourless, melts at 95°, and is very readily soluble in alcohol, ether, or benzene, but only slightly so in water; on hydrolysis, it forms *m*-bromo-*p*-toluidine melting at 26°. E. W. W.

**Production of Acylamines.** By FREDERICK L. DUNLAP (*J. Amer. Chem. Soc.*, 1902, 24, 758—763).—When 2 gram-mols. of sodium acetate are intimately mixed with 1 gram-mol. of aniline hydrochloride and the mixture is heated in sealed tubes at 165° for three hours, 71—72 per cent. of the theoretical yield of acetanilide is obtained. Variations in proportion of reacting ingredients or of temperature or time of heating diminishes the yield, as does also the substitution of calcium acetate for the sodium salt. By the same reaction, with appropriate reagents, acetyltoluidide, acetamide, benzoylanilide, benzamide, and methylbenzamide have been prepared, but formanilide could not be obtained by the action of sodium formate on aniline hydrochloride at 185°. T. A. H.

**Action of Phenylcarbimide on the Esters of some Oxyacids.** II. By EUGÈNE LAMBLING (*Bull. Soc. Chim.*, 1902, [iii], 27, 871—875. Compare this vol., i, 537, 603).—On heating together, at 175—178°, ethyl diethylglycollate and phenylcarbimide, the *phenylurethane* of *ethyl diethylglycollate*,  $\text{NHPh}\cdot\text{CO}\cdot\text{O}\cdot\text{CET}_2\cdot\text{CO}_2\text{Et}$ , is obtained, which crystallises from aqueous alcohol in slender needles melting at 68°; it is soluble in ether, chloroform, or benzene. On saponification with sodium hydroxide, it yields *diethyloxalanilide*, which crystallises in lozenge-shaped plates melting at 91°. Similarly, by heating ethyl benzilate with phenylcarbimide, there is obtained the *phenylurethane* of *ethyl benzilate*,  $\text{NHPh}\cdot\text{CO}\cdot\text{O}\cdot\text{CPh}_2\cdot\text{CO}_2\text{Et}$ ; it crystallises in slender, white needles, melts at 151° and is soluble in alcohol, ether, chloroform, or benzene. On boiling with excess of a solution of sodium hydroxide, it yields *benzilanilide*, which crystallises in microscopic prisms melting at 174—175°; it is insoluble in water, but soluble in alcohol, ether, chloroform, or benzene. The *phenylurethane* of *methyl salicylate*, obtained by heating methyl salicylate with phenylcarbimide, crystallises in white, microscopic needles melting at 96°. On saponification with sodium hydroxide, there is obtained *salicylanilide*, which crystallises in slender needles melting at 135°.

A. F.

**Some Derivatives of  $\beta$ -Naphthylamine.** By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1902, [iii], 27, 882—888).—*Ethyl- $\beta$ -naphthylamine camphorsulphonate*, formed by the direct union of the acid and base dissolved in ethyl acetate, forms white, compact crystals melting at  $117^\circ$ ; it dissolves in water but undergoes hydrolytic dissociation. *Diethyl- $\beta$ -naphthylamine hydriodide*, crystallised from a mixture of ethyl acetate and alcohol, forms hard, colourless prisms melting at  $152$ — $153^\circ$ . *Diethyl- $\beta$ -naphthylamine*, obtained by the action of alkali on the hydriodide, is an almost colourless liquid boiling at  $318$ — $319^\circ$ ; a dilute ether or benzene solution exhibits a slight violet fluorescence. The *hydrochloride* forms deliquescent crystals melting at  $177$ — $178^\circ$ . The *camphorsulphonate* could be obtained only as a gelatinous residue which refused to crystallise.

*Triethyl- $\beta$ -naphthylammonium iodide*, obtained by heating diethylnaphthylamine with a slight excess of ethyl iodide, crystallises in colourless, lustrous, striated, rectangular plates melting at  $174^\circ$ . *Trimethyl- $\beta$ -naphthylammonium iodide*, prepared by the repeated action of methyl iodide on  $\beta$ -naphthylamine, crystallises in colourless plates melting at  $190^\circ$  with intumescence. *Dimethyl- $\beta$ -naphthylamine* was obtained by distilling the quaternary base obtained from the iodide by the action of silver hydroxide; it forms a crystalline mass which melts at  $46^\circ$  and boils at  $304.5$ — $305^\circ$ . *Dimethyl- $\beta$ -naphthylamine hydrochloride* forms a felted mass of white, slender needles or colourless, non-deliquescent prisms melting at  $159^\circ$ . The *camphorsulphonate* forms colourless laminæ melting at  $115^\circ$ .  
A. F.

**Preparation of Aminohydroxyphenanthrenes.** By JULIUS SCHMIDT, and, in part, with A. KÄMPF (*Ber.*, 1902, 35, 3129—3133. Compare Pschorr, this vol., i, 672).—9-Amino-10-hydroxyphenanthrene may readily be obtained by the reduction of phenanthraquinonemonoxime with hydrogen sulphide, and isolated as its hydrochloride. When the hydrochloride is boiled with acetic anhydride, it yields *anhydroacetyl-9-amino-10-hydroxyphenanthrene*,  $C_{14}H_8N \cdot \text{Ac}$ , in the form of yellowish, glistening needles, melting at  $146$ — $147^\circ$  and dissolving in dilute mineral acids to deep blue solutions. The mother liquor from this anhydro-base yields Pschorr's 9-acetylamino-10-acetoxypheanthrene.

*Di-9-hydroxyphenanthryl-10-amine*,  $(\text{OH} \cdot C_{14}H_8)_2\text{NH}$ , is obtained when water is added to an alcoholic solution of the base produced by the reduction of phenanthraquinonemonoxime with hydrogen sulphide; it crystallises in glistening, brown prisms melting and decomposing at  $168$ — $170^\circ$ .

*3-Nitro-10-(or 9-)amino-9-(or 10-)hydroxyphenanthrene*, obtained by the reduction of 3-nitrophenanthraquinonemonoxime with alcoholic hydrogen sulphide, yields a *hydrochloride* crystallising in yellow needles. On treatment with aqueous solutions, it is converted into 3-nitro-9 : 10-dihydroxyphenanthrene.

A small amount of 3 : 10-(or 9-)diamino-9 (or 10-)hydroxyphenanthrene may be obtained when the nitroquinonemonoxime is very carefully reduced with stannous chloride. It forms reddish-yellow needles melting at  $264$ — $265^\circ$ .  
J. J. S.

**Nitration of 2-Aminofluorene.** By OTTO DIELS, EMIL SCHILL, and STANLEY TOLSON (*Ber.*, 1902, **35**, 3284—3290).—2-Acetylaminofluorene (Strassburger, *Abstr.*, 1884, 754), when nitrated in acetic acid solution, gives a mixture of two mononitro-compounds which it has not been possible to separate. On saponification, a mixture of two nitroaminofluorenes is obtained which can be separated on account of their different basicities. The less basic one, 1-nitro-2-aminofluorene,  $\text{NH}_2 \cdot \text{C}_{13}\text{H}_8 \cdot \text{NO}_2$ , melts at  $206^\circ$  (corr.), and is comparatively insoluble in alcohol, ether, or benzene, but soluble in acetic acid. It forms a hydrochloride which, however, suffers hydrolysis in water. When reduced with zinc and hydrochloric acid, it gives 1:2-diaminofluorene, which is a monoacidic base forming the hydrochloride  $\text{C}_{13}\text{H}_{12}\text{N}_2 \cdot \text{HCl}$ . The free base can be obtained from the hydrochloride by means of methylamine; it forms white crystals which melt at  $193^\circ$  (corr.), and an alcoholic solution becomes green when treated with ferric chloride. With diacetyl, the diamino-compound forms a quinoline derivative of the formula  $\text{C}_{17}\text{H}_{14}\text{N}_2$ , which crystallises in long, colourless needles.

The more basic nitro-compound, 7-nitro-2-aminofluorene, crystallises in orange-red prisms, melts at  $232^\circ$  (corr.), and is easily soluble in alcohol or acetic acid. When reduced with zinc and hydrochloric acid, it gives 2:7-diaminofluorene (Schultz, *Abstr.*, 1880, 814). J. McC.

**Molecular Rearrangement of Thiocyanacetanilides into Labile  $\psi$ -Thiohydantoin, and the Molecular Rearrangement of the Latter into Stable Isomerides.** By HENRY L. WHEELER and TREAT B. JOHNSON (*Amer. Chem. J.*, 1902, **28**, 121—158).—By the action of potassium thiocyanate on chloroacetanilides, Grothe (*Abstr.*, 1901, i, 80) obtained a series of compounds which he believed were thiocyanacetanilides,  $\text{NHR} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{SCN}$ . Frerichs and Beckurts (*Abstr.*, 1901, i, 80) repeated his experiments, and came to the conclusion that all his compounds, with the exception of the supposed thiocyanaceto-*p*-toluidide, were normal thiocyanates; they found however, that by the action of potassium thiocyanate on an alcoholic solution of chloroaceto-*p*-toluidide for only a short time, a labile compound, which they regarded as thiocarbiminoaceto-*p*-toluidide,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NCS}$ , was produced; they further observed that when the solution was warmed, this labile compound was rapidly converted into a substance supposed to be thiocyanaceto-*p*-toluidide, and that the latter was quickly changed into *p*-tolylthiohydantoin.

The present authors have prepared the thiocyanacetanilides according to Grothe's directions, and have found that although the aniline, *o*-toluidine, and *p*-xylydine compounds are correctly described, the so-called thiocyanaceto-*p*-toluidide and thiocyanacetyl-*p*-phenetide are neither thiocyan- nor thiocarbimino-derivatives; the *p*-toluidine compound is a labile  $\psi$ -thiohydantoin,  $\text{CO} \begin{array}{c} \text{CH}_2 \text{---} \text{S} \\ \diagup \quad \diagdown \\ \text{N}(\text{C}_6\text{H}_4\text{Me}) \cdot \text{C} : \text{NH} \end{array}$ , whilst the *p*-phenetidine compound is the stable *p*-phenetyl- $\psi$ -thiohydantoin,  $\text{CO} \begin{array}{c} \text{CH}_2 \cdot \text{S} \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{C} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt} \end{array}$ . The molecular rearrangement



of thiocyanacetanilides into the stable hydantoin does not involve the formation of a thiocarbimino-derivative at any stage.

Thiocyanacetanilide crystallises in colourless, acicular prisms and melts at about  $91^{\circ}$ ; if recrystallised from alcohol, it melts at  $86-88^{\circ}$ , and when crystallised from benzene it contains benzene of crystallisation which is rapidly lost on heating or on exposure to the air. By the action of the calculated quantity of thioacetic acid on it, *acetylthioglycollanilide*,  $\text{SAC} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$ , is produced, which crystallises from alcohol in colourless needles and melts at  $97-98^{\circ}$ ; the same compound may be obtained by the action of sodium thioacetate on chloroacetanilide. In two experiments, in which thiocyanacetanilide was heated with an excess of thioacetic acid, a *substance* (probably an acetyldithiourethane) was obtained which crystallises in slender needles and melts and decomposes at  $192^{\circ}$ ; in other experiments, a *dithiourethane*,  $\text{NH}_2 \cdot \text{CS} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$ , was produced which crystallises in square plates, melts at  $162^{\circ}$ , and is converted by the action of alkali hydroxide into alkali thiocyanate and a salt of thioglycollanilide. When thiocyanacetanilide is treated with sodium hydroxide, phenylthiohydantoic acid is formed melting at  $185-190^{\circ}$ . If thiocyanacetanilide is heated for a few minutes at its melting point, it is converted into the labile *phenyl- $\psi$ -thiohydantoin* (4-keto-2-

imino-3-phenyltetrahydrothiazole),  $\text{CO} < \begin{array}{c} \text{CH}_2 - \text{S} \\ | \\ \text{NPh} \cdot \text{C} \cdot \text{NH} \end{array}$ , which crystallises

from benzene in orthorhombic prisms [ $a:b:c = 0.97:1:1.35$ ] and melts at  $148^{\circ}$  to a blood-red liquid; its *hydrochloride* melts at  $192-193^{\circ}$  and the *picrate* at  $180^{\circ}$ . If the labile thiohydantoin is warmed with thioacetic acid, hydrogen sulphide is evolved and an

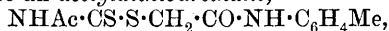
*acetyl* derivative,  $\text{CO} < \begin{array}{c} \text{CH}_2 - \text{S} \\ | \\ \text{NPh} \cdot \text{C} \cdot \text{NAc} \end{array}$ , is produced which melts at

$191-192^{\circ}$ ; the same compound may be obtained by the action of acetic anhydride on phenylthiohydantoic acid or on thiocyanacetanilide. The labile thiohydantoin is dissolved by sodium hydroxide with formation of phenylthiohydantoic acid. When the labile thiohydantoin is heated to  $165^{\circ}$ , it is converted into the stable phenyl- $\psi$ -

thiohydantoin,  $\text{CO} < \begin{array}{c} \text{CH}_2 - \text{S} \\ | \\ \text{NH} \cdot \text{C} \cdot \text{NPh} \end{array}$ , which forms triclinic crystals

[ $a:b:c = 1.508:1:0.859$ ;  $\alpha = 108^{\circ}25'$ ,  $\beta = 113^{\circ}15'$ ,  $\gamma = 96^{\circ}35'$ ]; the *hydrochloride* melts at  $203^{\circ}$  and the *diacetyl* derivative at  $161-162^{\circ}$ . By the action of benzyl chloride on the sodium salt of the stable thiohydantoin, phenylbenzylthiohydantoin is produced melting at  $124-125^{\circ}$ .

Thiocyanaceto-*o*-toluidide melts at  $102-103^{\circ}$  as stated by Grothe, but if warmed with ether for two hours or repeatedly crystallised from benzene it melts at about  $109^{\circ}$ . By the action of thioacetic acid, it is converted into an *acetyldithiourethane*,



which melts and decomposes at about  $200^{\circ}$ . Thiobenzoic acid reacts with thiocyanaceto-*o*-toluidide to form *benzoylthioglycoll-*o*-toluidide*, which crystallises in long needles and melts at  $141-142^{\circ}$ . When thiocyanaceto-*o*-toluidide is treated with alkali hydroxide, *o*-tolylcyanamide is produced. By heating thiocyanaceto-*o*-toluidide for

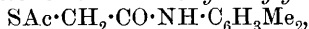
half-an-hour at  $110^{\circ}$ , *o*-tolylthiohydantoic acid is obtained together with the labile *o*-tolyl- $\psi$ -thiohydantoin; the latter compound melts at  $131$ — $132^{\circ}$  and is thereby converted into the stable *o*-tolyl- $\psi$ -thiohydantoin described by Dixon (Trans., 1897, 71, 623). When the stable hydantoin is heated with acetic anhydride, a *diacetyl* derivative is formed melting at  $91$ — $92^{\circ}$ . *o*-Tolylthiohydantoic acid crystallises in thin plates and melts and decomposes between  $208^{\circ}$  and  $230^{\circ}$ . *o*-Tolylthiocarbamide melts at  $162^{\circ}$ , and not at  $155^{\circ}$  as stated by Staats (Abstr., 1880, 386).

Thiocyanoaceto-*p*-toluidide,  $C_6H_4Me \cdot NH \cdot CO \cdot CH_2 \cdot SCN$ , forms acicular prisms and melts at  $85^{\circ}$ . By the action of thioacetic acid, it is converted into a *dithiourethane*,  $C_6H_4Me \cdot NH \cdot CO \cdot CH_2 \cdot S \cdot CS \cdot NH_2$ . When heated above its melting point, labile *p*-tolyl- $\psi$ -thiohydantoin is produced, which melts at  $125$ — $126^{\circ}$ ; its *acetyl* derivative crystallises in colourless plates and melts at  $175$ — $176^{\circ}$ . If the labile thiohydantoin is treated with alkali hydroxide, *p*-tolylthiohydantoic acid is formed, which melts and decomposes at  $210$ — $212^{\circ}$ . The stable *p*-tolyl- $\psi$ -thiohydantoin, obtained by heating the labile form for a short time at a temperature near its melting point, crystallises in needles and melts at  $183^{\circ}$ ; its *sodium* salt forms thin plates, and its *diacetyl* derivative crystallises in pale yellow prisms and melts at  $163$ — $164^{\circ}$ .

Labile *α-o*-xylyl- $\psi$ -thiohydantoin melts at  $111^{\circ}$ ; by the action of thioacetic acid it is converted into the stable hydantoin melting at  $179^{\circ}$ . *α-o*-Xylylthiohydantoic acid, formed in the preparation of the labile hydantoin, melts and decomposes at about  $208^{\circ}$ .

Thiocyanoacetyl-*p*-xylylide,

$C_6H_3Me_2 \cdot NH \cdot CO \cdot CH_2 \cdot SCN$  [ $Me : NH : Me = 1 : 2 : 4$ ], is converted by thioacetic acid into *acetylthioglycoll-p*-xylylide,



which crystallises in colourless prisms and melts at  $139$ — $140^{\circ}$ . By the action of sodium hydroxide on thiocyanoacetyl-*p*-xylylide, *p*-xylyl-cyanamide is produced which melts at  $118^{\circ}$ . When thiocyanoacetyl-*p*-xylylide is boiled with ether for one to two hours, the labile *p*-xylyl- $\psi$ -thiohydantoin is obtained, which crystallises in needles, melts at  $109$ — $110^{\circ}$ , and is converted by alkali hydroxide into *p*-xylylcyanamide. *p*-Xylylthiohydantoic acid,  $C_6H_3Me_2 \cdot N(NH_2) \cdot CS \cdot CH_2 \cdot CO_2H$ , decomposes at about  $200^{\circ}$ , and when dissolved in alkali hydroxide yields *p*-xylylcyanamide. The stable *p*-xylyl- $\psi$ -thiohydantoin crystallises in minute prisms and melts at  $161$ — $162^{\circ}$ .

Labile *p*-phenetyl- $\psi$ -thiohydantoin melts at  $128^{\circ}$  and is converted by thioacetic acid into the *acetyl* derivative, which crystallises in needles or prisms and melts at  $155^{\circ}$ . When the labile hydantoin is heated at  $140$ — $145^{\circ}$  for half-an-hour, the stable form is produced which melts at  $163$ — $164^{\circ}$ . *p*-Phenetylthiohydantoic acid melts and decomposes at  $212^{\circ}$ .

E. G.

Thiocyanates and *iso*Thiocyanates (Thiocarbimides). IV. By HENRY L. WHEELER and TREAT B. JOHNSON (*J. Amer. Chem. Soc.*, 1902, 24, 680—690. Compare Abstr., 1902, i, 28, 537).— $\beta$ -Bromoisobutane reacts with potassium thiocyanate to form  $\beta$ -thiocyanoisobutane, a colourless, pungent oil, which, with thioacetic acid, is con-

verted into *isobutyl acetyldithiocarbamate*,  $\text{NHAc} \cdot \text{CS}_2 \cdot \text{CMe}_3$ , forming yellow crystals melting at  $112\text{--}113^\circ$ , and a second substance crystallising in colourless plates from benzene.

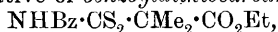
$\alpha$ -*Bromoisopropylbenzene*, prepared by brominating the hydrocarbon at  $115\text{--}120^\circ$ , reacts with potassium thiocyanate to form  $\psi$ -cyanogen sulphide and an oil of unknown composition. *Diphenylbromoethane*,  $\text{CPh}_2\text{BrMe}$ , prepared by brominating the hydrocarbon at  $100\text{--}105^\circ$ , decomposes when heated in a vacuum into hydrogen bromide and diphenylethylene. The latter, together with  $\psi$ -cyanogen sulphide, is also produced by the action of potassium thiocyanate.

Methyl  $\alpha$ -bromohydratropate,  $\text{CMePhBr} \cdot \text{CO}_2\text{Me}$ , prepared by brominating the ester at  $150^\circ$ , is an oil which decomposes when heated in a vacuum. It reacts with potassium thiocyanate forming an oil of unknown composition and  $\psi$ -cyanogen sulphide. The latter also results from the interaction of potassium thiocyanate and *tricarbethoxymethyl bromide*, a colourless oil, which boils at  $162\text{--}165^\circ$  under 16 mm. pressure and is obtained by brominating tricarbethoxymethane at  $100^\circ$ .

Ethyl bromomethylmalonate, when warmed with alcoholic potassium thiocyanate, yields *ethyl thiocyanomethylmalonate*,  $\text{NCS} \cdot \text{CMe}(\text{CO}_2\text{Et})_2$ , a pungent oil which boils at  $139\text{--}142^\circ$  under 9 mm. pressure. With thioacetic acid in benzene solution, it furnishes 4-keto-2-thio-5-methylthiazolidine,  $\begin{array}{c} \text{S} \text{---} \text{CS} \\ | \quad \diagup \\ \text{CHMe} \cdot \text{CO} \end{array} \text{NH}$

*Ethyl phenylbromomalonate*,  $\text{CPhBr}(\text{CO}_2\text{Et})_2$ , obtained by brominating the ester at  $140\text{--}150^\circ$ , is a colourless oil which boils at  $192^\circ$  under 20 mm. and at  $177\text{--}178^\circ$  under 11 mm. pressure. With potassium thiocyanate, it yields *ethyl phenylthiocyanomalonate*, a colourless oil, which reacts with thioacetic acid to form 4-keto-2-thio-5-phenylthiazolidine. This crystallises in yellow prisms and melts at  $178\text{--}179^\circ$ .

Ethyl thiocyanoisobutyrate reacts with thiobenzoic acid to form the *ethyl isobutyrate* derivative of *benzoyldithiocarbamate*,



which crystallises from a mixture of petroleum and benzene in yellow prisms, melts at  $113\text{--}114^\circ$ , and dissolves readily in alcohol.

Ethyl diphenylchloroacetate, when treated with potassium thiocyanate, yields *ethyl diphenylthiocyanoacetate*. The latter does not react with thioacetic or thiobenzoic acids, but with aniline is converted into

*triphenyl- $\psi$ -thiohydantoin*,  $\begin{array}{c} \text{S} \cdot \text{C}(\text{NPh}) \\ | \quad \diagup \\ \text{CPh}_2 \text{---} \text{CO} \end{array} \text{NH}$ , which crystallises from alcohol in colourless prisms and melts at  $250^\circ$ . This, with hydrochloric acid, is converted into 2:4-diketo-5-diphenyltetrahydrothiazole,

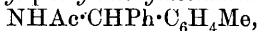
$\begin{array}{c} \text{S} \text{---} \text{CO} \\ | \quad \diagup \\ \text{CPh}_2 \cdot \text{CO} \end{array} \text{NH}$ , which crystallises in colourless prisms from alcohol and melts at  $144\text{--}145^\circ$ .

Ethyl phenylchloroacetate, when treated with phenylthiocarbamide, yields diphenyl- $\psi$ -thiohydantoin identical with that previously obtained by the interaction of aniline and ethyl phenylthiocyanoacetate (*loc. cit.*). When treated with hydrochloric acid, the diphenyl- $\psi$ -thiohydantoin furnishes 2:4-diketo 5:3-diphenyltetrahydrothiazole as white needles which melt at  $173\text{--}174^\circ$ . Benzylphenyl- $\psi$ -thiohydantoin (compare

Dixon, Trans., 1897, 71, 620) results when phenyl- $\psi$ -thiohydantoin is treated with benzyl chloride in presence of sodium ethoxide, or when benzylphenylthiocarbamide is warmed with ethyl chloroacetate and therefore has the formula  $\text{CH}_2 \begin{smallmatrix} \text{S} - \text{C} \cdot \text{NPh} \cdot \text{CH}_2\text{Ph} \\ \text{CO} \cdot \text{N} \end{smallmatrix}$ , which confirms that proposed by Dixon (*loc. cit.*) for the parent phenyl- $\psi$ -thiohydantoin.

T. A. H.

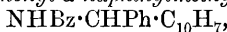
**Thiocyanates and isoThiocyanates (Thiocarbimides).** V. By HENRY L. WHEELER and GEORGE S. JAMIESON (*J. Amer. Chem. Soc.*, 1902, 24, 743—754. Compare Abstr., 1901, i, 514, and 1902, i, 28).—*Phenyl-p-tolylmethyl bromide*,  $\text{CMePhBr} \cdot \text{C}_6\text{H}_4\text{Me}$ , obtained by the action of dry hydrogen bromide on phenyl-*p*-tolylcarbinol at  $100^\circ$ , is a thin, red oil, which reacts in benzene solution with potassium thiocyanate to form *phenyl-p-tolylmethylthiocarbimide*,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{CHPh} \cdot \text{NCS}$ , a mobile, reddish-coloured oil giving off irritating vapours. This reacts with thioacetic acid to form *phenyl-p-tolylmethylacetamide*,



which crystallises from ether in flat, rectangular prisms and melts at  $129.5\text{--}131^\circ$ . The thiocarbimide reacts with alcoholic ammonia, aniline, and  $\beta$ -naphthylamine to form respectively *phenyl-p-tolylmethylthiocarbimide*,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{CHPh} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH}_3$ , separating in rosettes of colourless needles which melt at  $162\text{--}163^\circ$ , *phenyl-p-tolylmethylphenylthiocarbimide*,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{CHPh} \cdot \text{NH} \cdot \text{CS} \cdot \text{NHPh}$ , crystallising from alcohol in flat prisms which melt at  $159^\circ$ , and *phenyl-p-tolylmethyl- $\beta$ -naphthylthiocarbimide*,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{CHPh} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7$ , crystallising from alcohol in slender needles and melts at  $170^\circ$ .

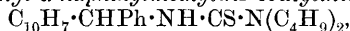
*p-Benzyltolyl bromide*, prepared by brominating the hydrocarbon at  $130\text{--}135^\circ$ , is a heavy, yellowish oil which boils at  $179\text{--}180^\circ$  under 11 mm. pressure. Potassium thiocyanate converts it into the corresponding *thiocyanate*. This, however, with ammonia and  $\beta$ -naphthylamine, gives small quantities of the thiocarbimides described in the preceding paragraph.

*Phenyl- $\alpha$ -naphthylmethyl bromide* reacts with potassium thiocyanate to form the corresponding *thiocarbimide*,  $\text{C}_{10}\text{H}_7 \cdot \text{CHPh} \cdot \text{NCS}$ , which crystallises in small plates melting at  $76\text{--}77^\circ$ . With thioacetic and thiobenzoic acids, respectively, this furnishes *phenyl- $\alpha$ -naphthylmethylacetamide*,  $\text{NHAc} \cdot \text{CHPh} \cdot \text{C}_{10}\text{H}_7$ , which crystallises in small needles and melts at  $210^\circ$ , and *phenyl- $\alpha$ -naphthylmethylbenzamide*,



which melts at  $158^\circ$ . The thiocarbimide reacts in the usual manner with ammonia and amines and the following thiocarbimides were thus prepared.

*Phenyl- $\alpha$ -naphthylmethylthiocarbimide*,  $\text{C}_{10}\text{H}_7 \cdot \text{CHPh} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH}_3$ , forming rectangular prisms which melt at  $197\text{--}198^\circ$ ; *phenyl- $\alpha$ -naphthylmethylmethylthiocarbimide*,  $\text{C}_{10}\text{H}_7 \cdot \text{CHPh} \cdot \text{NH} \cdot \text{CS} \cdot \text{NHMe}$ , crystallising in prisms which melt at  $175\text{--}176^\circ$ ; *phenyl- $\alpha$ -naphthylmethyl-diethylthiocarbimide*,  $\text{C}_{10}\text{H}_7 \cdot \text{CHPh} \cdot \text{NH} \cdot \text{CS} \cdot \text{NEt}_2$ , forming flat prisms which melt at  $112\text{--}113^\circ$ ; *phenyl- $\alpha$ -naphthylmethyl-di-n-butylthiocarbimide*,



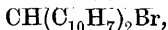
which melts at  $142\text{--}143^\circ$ ; *phenyl- $\alpha$ -naphthylmethylphenylthiocarbimide*,

$C_{10}H_7 \cdot CHPh \cdot NH \cdot CS \cdot NPh$ , forming colourless prisms which melt at  $185^\circ$ ; *phenyl- $\alpha$ -naphthylmethylphenylmethylthiocarbamide*,

$C_{10}H_7 \cdot CHPh \cdot NH \cdot CS \cdot NPhMe$ , which melts at  $182-183^\circ$ ; *phenyl- $\alpha$ -naphthylmethyl-m-chlorophenylthiocarbamide*,  $C_{10}H_7 \cdot CHPh \cdot NH \cdot CS \cdot NH \cdot C_6H_4Cl$ , crystallising in acicular prisms which melt at  $172-173^\circ$ ; *phenyl- $\alpha$ -naphthylmethyl-m-nitrophenylthiocarbamide*,  $C_{10}H_7 \cdot CHPh \cdot NH \cdot CS \cdot NH \cdot C_6H_4 \cdot NO_2$ , forming light yellow prisms which melt at  $191^\circ$ ; and *phenyl- $\alpha$ -naphthylmethyl- $\beta$ -naphthylthiocarbamide*,  $C_{10}H_7 \cdot CHPh \cdot NH \cdot CS \cdot NH \cdot C_{10}H_7$ , crystallising in needles which melt at  $195^\circ$ .

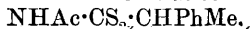
The thiocarbimide also reacts with phenylhydrazine to form *phenyl- $\alpha$ -naphthylmethylphenylthiosemicarbazide*, which melts first at  $154^\circ$ , then solidifies when further heated and remelts at  $174-175^\circ$ . After recrystallisation from alcohol, it melts at  $178-179^\circ$ . The transformation occurring is represented thus:  $C_{10}H_7 \cdot CHPh \cdot NH \cdot CS \cdot NPh \cdot NH_2 \rightarrow C_{10}H_7 \cdot CHPh \cdot NH \cdot CS \cdot NH \cdot NPh$  (compare Busch and Holzmänn, Abstr., 1901, i, 234).

Di- $\alpha$ -naphthylmethane,  $CH_2(C_{10}H_7)_2$ , prepared by condensing naphthalene with chloromethyl acetate in presence of zinc chloride, when brominated at  $135-145^\circ$  furnishes *di- $\alpha$ -naphthylmethyl bromide*,



which crystallises from benzene in acicular prisms, melts at  $181-182^\circ$ , is readily soluble in chloroform, but less so in light petroleum. This reacts with potassium thiocyanate to form *di- $\alpha$ -naphthylmethylthiocarbimide*,  $CH(C_{10}H_7)_2 \cdot NCS$ , which crystallises from alcohol in rectangular prisms and melts at  $124-125^\circ$ . With aniline, methylaniline, and naphthylamine, it reacts to form, respectively, *di- $\alpha$ -naphthylmethylphenylthiocarbamide*,  $CH(C_{10}H_7)_2 \cdot NH \cdot CS \cdot NPh$ , which crystallises in needles and melts at  $225-226^\circ$ ; *di- $\alpha$ -naphthylmethylphenylmethylthiocarbamide*,  $CH(C_{10}H_7)_2 \cdot NH \cdot CS \cdot NPhMe$ , forming needles which melt at  $210-211^\circ$ ; and *di- $\alpha$ -naphthylmethyl- $\beta$ -naphthylthiocarbamide*,  $CH(C_{10}H_7)_2 \cdot NH \cdot CS \cdot NH(C_{10}H_7)$ , which crystallises in spherical masses of needles and melts at  $218-219^\circ$ .

Thiocyanoethylbenzene,  $CHMePh \cdot SCN$ , reacts with thioacetic acid to form the *ethylbenzene derivative of dithiocarbamic acid*,



which crystallises in slender, yellow prisms and melts at  $99-100^\circ$ .

With thiobenzoic acid, isopropyl thiocyanate forms *benzoyldithioisopropylcarbamate*,  $NHBz \cdot CS_2Pr$ . This crystallises in brilliant, yellow plates and melts at  $74-75^\circ$ .

Bromodinaphthaxanthone does not react with potassium thiocyanate, whence the author prefers for this substance the formula proposed by Werner (Abstr., 1902, i, 50) rather than that suggested by Fosse (Abstr., 1901, i, 604).

T. A. H.

**Thiocyanoacetic Acids and Thio-fatty Anilides.** By HEINRICH BECKURTS and GUSTAV FRERICHS (*J. pr. Chem.*, 1902, [ii], 66, 172-193. Compare Abstr., 1900, i, 478; 1901, i, 80).—When boiled with water, carbaminethioglycollanilide yields thioglycollanilide and cyanic acid, the formation of carbon dioxide and ammonia being due to hydrolysis of the cyanic acid (compare Rizzo, Abstr., 1898, i, 659).

The formation of cyanic acid is determined by conversion into carbamide. The formation of diphenylcarbamide when carbaminethioglycollanilide is treated with aniline, and the formation of methylthioglycollanilide when the carbamine is heated with methyl iodide and sodium methoxide (Rizzo), are explained by the decomposition of the carbamine into thioglycollanilide and cyanic acid when warmed with alkalis or organic bases. The decomposition also takes place when the carbamine is heated above its melting point.

Thioglycollanilide melts at 111—112° (Rizzo, m. p. 105—107°) and is best obtained by warming the carbamine with alcoholic ammonia (compare Liebermann, *Annalen*, 1881, 207, 129). A small part of the product is oxidised to dithiodiglycollanilide, which is insoluble in alcohol.

Grothe's compounds (Abstr., 1901, i, 80) are formed when chloroacetanilides are heated with potassium thiocyanate in alcoholic solution for 15 minutes. When chloroacetanilide is heated with potassium thiocyanate in alcoholic solution for several hours, phenylthiohydantoin (m. p. 178°) is formed (compare Rizzo, *loc. cit.*).

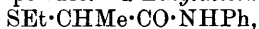
When warmed with fuming hydrochloric acid, the thiocyanacetanilides are converted into carbaminethioglycollanilides. Thiocarbiminoacetylmethylanilide melts at 79° (Grothe, m. p. 69°), and is converted by fuming hydrochloric acid into carbaminethioglycollmethylanilide,  $\text{CN}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NMePh}$ , which crystallises in glistening leaflets and melts at 147°.

The following derivatives of the thio-fatty anilides are described. Dithiodiglycollanilide melts at 160—161° (Rizzo, m. p. 165°) and is best prepared by oxidation of thioglycollanilide with ferric chloride in alcoholic solution. Thioglycollanilide yields a copper derivative,  $\text{Cu}_2(\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh})_2$ , as an amorphous, yellow powder. Ethylthioglycollanilide,  $\text{SEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$ , prepared by the action of ethyl iodide and potassium hydroxide in alcoholic solution, forms colourless leaflets, melts at 61°, and is easily soluble in alcohol, but insoluble in water. Dimethylmethylenedithioglycollanilide,  $\text{CMe}_2(\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh})_2$ , formed by the action of hydrogen chloride on thioglycollanilide dissolved in acetone, crystallises from alcohol in colourless needles, melts at 170°, is soluble in hot, more sparingly so in cold, alcohol, and insoluble in water. Thiodiglycollanilide, formed by the action of potassium hydroxide on thioglycollanilide and chloroacetanilide in alcoholic solution, crystallises from alcohol in delicate needles and melts at 166—167° (Rizzo, *loc. cit.*, m. p. 160—161°; Anschütz and Biernaux, Abstr., 1893, i, 191, m. p. 168°). Carboxyethylthioglycollanilide,  $\text{CO}_2\text{Et}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$ , formed by the action of potassium hydroxide and ethyl chlorocarbonate on thioglycollanilide, crystallises from alcohol in flat, colourless needles and melts at 99°.  $\alpha$ -Carbaminethiolactanilide,



formed by the action of potassium thiocyanate on  $\alpha$ -bromopropionic acid and aniline in alcoholic solution, crystallises in glistening leaflets, melts at 117°, and is easily soluble in alcohol, insoluble in water.  $\alpha$ -Thiolactanilide,  $\text{SH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NHPh}$ , formed by the action of ammonia on the carbamine, crystallises in colourless leaflets and melts at 91°.  $\alpha$ -Dithiodilactanilide,  $\text{S}_2(\text{CHMe}\cdot\text{CO}\cdot\text{NHPh})_2$ , obtained by oxidation of thiolactanilide with ferric chloride in alcoholic solution, crystallises in colourless needles

and melts at  $160^{\circ}$ . The *copper* derivative,  $\text{Cu}_2(\text{S}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NHPH})_2$ , forms a greenish-yellow powder.  *$\alpha$ -Ethylthiolactanilide*,



crystallises in colourless leaflets and melts at  $97^{\circ}$ .  *$\alpha$ -Carbaminethiobutyranilide*,  $\text{NH}_2\cdot\text{CO}\cdot\text{S}\cdot\text{CHEt}\cdot\text{CO}\cdot\text{NHPH}$ , crystallises in colourless leaflets, melts at  $120^{\circ}$ , is easily soluble in alcohol, and insoluble in water.  *$\alpha$ -Thiobutyranilide*,  $\text{SH}\cdot\text{CHEt}\cdot\text{CO}\cdot\text{NHPH}$ , crystallises in delicate, colourless needles and melts at  $95^{\circ}$ .  *$\alpha$ -Dithiodibutyranilide*,  $\text{S}_2(\text{CHEt}\cdot\text{CO}\cdot\text{NHPH})_2$ , crystallises from dilute alcohol in delicate, colourless needles and melts at  $110^{\circ}$ . The *copper* derivative,  $\text{Cu}_2(\text{S}\cdot\text{CHEt}\cdot\text{CO}\cdot\text{NHPH})_2$ , forms a yellow, amorphous powder.  *$\alpha$ -Ethylthiobutyranilide*,  $\text{SEt}\cdot\text{CHEt}\cdot\text{CO}\cdot\text{NHPH}$ , crystallises in delicate, colourless needles and melts at  $68^{\circ}$ . G. Y.

**Hydroxamic Acids.** By ANGELO ANGELI, FRANCESCO ANGELICO, and F. SCURTI (*Atti Real. Accad. Lincei*, 1902, [v], 11, i, 555—561).—The products of hydrolysis of most compounds, such as esters, amides, &c., are usually the same whether the decomposition is brought about by means of acids or alkalis, but with hydroxylaminesulphonic acids, benzenesulphohydroxamic, and nitrohydroxylaminic acids, this is not the case. Thus, with alkalis, these compounds yield a nitroxyl group and the corresponding acid, either sulphurous acid or a sulphinic acid,  $\text{RHSO}_2$ , and nitrous acid. With acids, however, the first two of the above compounds yield hydroxylamine together with sulphuric acid or a sulphonic acid,  $\text{R}\cdot\text{SO}_3\text{H}$ , whilst nitrohydroxylaminic acid loses immediately a mol. of water and gives nitrogen dioxide.

To obtain further information as to the mechanism of this hydrolytic action, the authors have prepared and studied hydroxamic acids of sulphur of the following types, which readily lend themselves to such decomposition:  $\text{R}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{OH}$ ;  $\text{R}\cdot\text{SO}_2\cdot\text{NR}^1\cdot\text{OH}$ ;  $\text{R}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{OR}^1$ ;  $\text{R}\cdot\text{SO}_2\cdot\text{NR}^1\cdot\text{OR}^2$ ; R representing an aliphatic or aromatic residue and  $\text{R}^1$  and  $\text{R}^2$  aromatic, aliphatic, or acid residues. The acids studied of the first type, namely,  $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{NH}\cdot\text{OH}$ ;  $\text{SO}_2\text{Et}\cdot\text{NH}\cdot\text{OH}$ ;  $\text{C}_6\text{H}_4(\text{SO}_2\cdot\text{NH}\cdot\text{OH})_2$ ; and  $\text{C}_{10}\text{H}_6(\text{SO}_2\cdot\text{NH}\cdot\text{OH})_2$ , which are analogous to the acid prepared by Piloty (*Abstr.*, 1896, i, 555), behaves similarly to benzenesulphohydroxamic acid. The alkaline hydrolysis was carried out in presence of either an aldehyde or nitrosobenzene, the nitroxyl group split off being thus converted into either a hydroxamic acid or nitrosophenylhydroxylamine. In the case, however, of  $\alpha$ -naphthalenesulphohydroxamic acid, the residue, after the removal of nitroxyl, undergoes molecular rearrangement, yielding  $\beta$ -naphthalenesulphinic acid.

When sulphohydroxamic acids in which two atoms of hydrogen are replaced by acid radicles, for instance,  $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{NAc}\cdot\text{OAc}$  and  $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{NAc}\cdot\text{OAc}$ , are hydrolysed in presence of alkali they exhibit a similar behaviour to the above. The same is the case with the acid,  $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{NPh}\cdot\text{OH}$ , which yields benzenesulphinic acid and nitrosobenzene (corresponding with the nitroxyl residue) and with  $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{N}(\text{CH}_2\text{Ph})\cdot\text{OH}$ , which gives nitrosotoluene, this soon undergoing transformation into benzaldehyde.

The above behaviour is explained by supposing that in alkaline

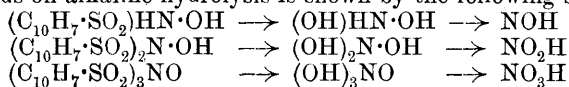
solution these compounds react as if they possessed the tautomeric structure  $R \cdot SO(OH) : NOH$ .

Substituted hydroxamic acids of the type  $R \cdot SO_2 \cdot NH \cdot OR^1$ , where  $R^1$  represents an alcoholic residue, do not, however, exhibit such a reaction. Thus the acid  $C_6H_5 \cdot SO_2 \cdot NH \cdot O \cdot CH_2Ph$  can be precipitated unchanged from solution in alkali, even after long heating.

The authors have prepared dibenzenesulphohydroxamic acid, which they find to melt at  $126^\circ$ , although Koenigs (Abstr., 1878, 573) and Piloty (*loc. cit.*) gave the melting point  $109^\circ$ . With alkalis, this acid yields benzenesulphinic acid and nitrous acid, whilst with sulphuric acid it gives hydroxylamine. The corresponding naphthalene derivative,  $OH \cdot N(SO_2 \cdot C_{10}H_7^a)_2$ , when treated with alkalis, likewise gives nitrous acid and a sulphinic acid, the latter being, however, the  $\beta$ -compound, namely,  $\beta$ -naphthalenesulphinic acid; if now the liquid be acidified, the latter acid reacts with the nitrous acid, giving di- $\beta$ -naphthalenesulphohydroxamic acid,  $OH \cdot N(SO_2 \cdot C_{10}H_7^\beta)_2$ . The nitrous acid formed in this alkaline hydrolysis is obtained by the splitting off of water from the radicle  $N(OH)_3$ , so that in this case, as also in those given above, each sulphonic group attached to the nitrogen atom is replaced by a hydroxyl group.

This also happens in the alkaline hydrolysis of tribenzenesulphohydroxylamine,  $(Ph \cdot SO_2)_3NO$ , in which nitric acid is formed.

The analogy existing between the behaviour of these various compounds on alkaline hydrolysis is shown by the following scheme:



T. H. P.

**The Methyl Ethers of the True Nitrosophenols.** *o*-Nitrosophenol By ADOLF VON BAEYER and EDUARD KNORR (*Ber.*, 1902, 35, 3034—3037).—The *o*- and *p*-nitrosoanisoles can readily be prepared by the action of Caro's reagent on the corresponding anisidines. *p*-Nitrosoanisole has not been obtained quite free from nitroanisole, but the impure compound crystallises in large, bluish-green prisms, melting at about  $32$ — $34^\circ$ , forms bluish-green solutions in all organic solvents except light petroleum, readily volatilises in steam, and decomposes in the air. Dilute acids and alkalis readily hydrolyse it with formation of *p*-nitrosophenol. *o*-Nitrosoanisole is not accompanied by the nitro-compound and can readily be obtained pure; it crystallises in colourless, six-sided plates, melts at  $103^\circ$ , is stable in the air, dissolves to some extent in cold, and more readily in hot, water, forming green solutions, and is readily volatile in steam. It is only slowly attacked, even by concentrated aqueous potash, whilst acids convert it into a resinous mass.

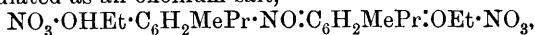
*o*-Nitrosophenol (*o*-quinoneoxime), can be prepared from *o*-nitrosoanisole by gradually adding an aqueous solution of the latter to boiling aqueous potassium hydrogen sulphate. The free nitrosophenol has hitherto only been obtained as an oil. The sodium salt crystallises in dark red plates with a green surface lustre, and decomposes explosively when heated. The barium salt is sparingly soluble in water; the



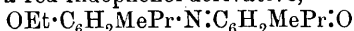
*silver* salt is a heavy, microcrystalline, almost black precipitate, which decomposes explosively when heated or brought into contact with a drop of sulphuric acid or fuming nitric acid. The properties of this *o*-nitrosophenol seem to indicate that it is an *o*-quinoneoxime.

A. H.

**Nitrosophenol Dyes. I.** By HERMANN DECKER and BASIL VON SOLONINA (*Ber.*, 1902, 35, 3217—3225).—The blue compound formed by the action of fuming nitric acid on thymol ethyl ether (Kehrmann and Messinger, *Ber.*, 1901, 34, 1626) was obtained in thin plates belonging to the rhombic system and melting constantly at 62—63°; it is formulated as an oxonium salt,

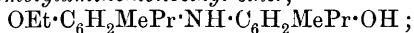


two alternative formulæ being also given. When dissolved in chloroform, it passes into a red indophenol derivative,

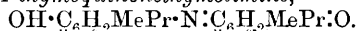


or  $\text{OEt} \cdot \text{C}_6\text{H}_2\text{MePr} \cdot \text{NO} : \text{C}_6\text{H}_2\text{MePr} \cdot \text{O}$ . This compound gives Liebermann's reaction with sulphuric acid, being thereby converted into a compound,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{MePr} \cdot \text{N} : \text{C}_6\text{H}_2\text{MePr} \cdot \text{O}$ .

The blue oxonium salt is reduced by sulphurous acid, hydrogen sulphide, or stannous chloride to *dithymolylamine diethyl ether*,  $\text{NH}(\text{C}_6\text{H}_2\text{MePr} \cdot \text{OEt})_2$ ; this separates from alcohol in beautiful, colourless crystals belonging to the triclinic system, melts at 70—71°, distils in part without decomposition, dissolves in acids, is not acted on by alkalis, and gives an intense indophenol reaction with concentrated sulphuric acid. The *hydrochloride*,  $\text{C}_{24}\text{H}_{30}\text{O}_2\text{NCl}$ , forms white needles and gradually oxidises in air to a red compound. *Thymoquinone thymol-iminoether*,  $\text{OEt} \cdot \text{C}_6\text{H}_2\text{MePr} \cdot \text{N} : \text{C}_6\text{H}_2\text{MePr} \cdot \text{O}$ , prepared by oxidising the preceding compound with ferric chloride, crystallises from alcohol, melts at 96—97°, has a dark red colour, is insoluble in water or alkalis, and dissolves in organic solvents with a deep violet-red colour. It is reduced by sulphurous acid, hydrogen sulphide, or stannous chloride to *dithymolylaminomonoethyl ether*,



this was not isolated, but was hydrolysed, in the manner usual with an indophenol, to thymoquinone and an aminophenol sulphate. Hydrogen iodide reduces the indophenol ether in a similar manner to that just described, but also hydrolyses it to *dithymolylamine*,  $\text{NH}(\text{C}_6\text{H}_2\text{MePr} \cdot \text{OH})_2$ ; the *hydriodide* of this was obtained in colourless crystals; the *base* dissolves in alkalis to a colourless solution which is at once oxidised in the air and deposits dark blue, glistening crystals of a salt of *thymoquinonethymolimine*,



The series of changes here described proves the constitution of the dithymolylamine diethyl ether, and renders probable the formula assigned to the original blue salt.

T. M. L.

**Partial and Complete Reduction Products of 2:6-Dinitrothymyl Ethyl Ether.** By G. OTTO GAEBEL (*Ber.*, 1902, 35, 2793—2802).—Ethyl-2:6-dinitrothymyl ether is most conveniently obtained by treating the silver derivative of 2:6-dinitrothymol with ethyl iodide in alcoholic solution.

2-Nitro-6-aminothymyl ethyl ether,  $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \text{CMe} \cdot \text{C}(\text{NO}_2) \\ \text{CH} \text{---} \text{CPr} \end{smallmatrix} \text{C} \cdot \text{OEt}$ ,

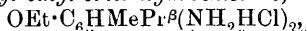
produced by reducing the dinitro-compound either with alcoholic ammonium sulphide or with the calculated amount of stannous chloride in alcoholic solution, crystallises from this solvent in rhombic plates melting at 111—112°; the *hydrochloride* separates from dilute hydrochloric acid in white needles melting at 195° and decomposing at 200°; the *sulphate* forms white, silky needles; the *acetyl* and *benzoyl* derivatives separate from dilute alcohol in white needles and melt at 119° and 138° respectively. The amino-ether, when treated with bromine dissolved in carbon disulphide, yields a *bromo-derivative* crystallising from dilute alcohol or ether in yellow, rhombic plates melting at 75°. The *hydrochloride* separates in white needles on passing hydrogen chloride into the ethereal solution of the bromo-compound; it is dissociated by water and decomposes at 156°.

The *benzoyl* derivative,  $\text{OEt} \cdot \text{C}_6\text{H}_4\text{MePr}^\beta(\text{NO}_2) \cdot \text{NHbz}$ , crystallises from dilute alcohol in white, quadratic plates and melts at 171°.

When 6-amino-2-nitrothymyl ethyl ether is diazotised with sodium nitrite and sulphuric acid in alcoholic solution, it yields an oily product which is probably a nitrothymyl ether, because, on reduction, it yields 2-aminothymyl ethyl ether,  $\text{OEt} \cdot \text{C}_6\text{H}_4\text{MePr}^\beta \cdot \text{NH}_2$ , which is characterised by means of its *hydrochloride*, a salt crystallising from dilute hydrochloric acid in white needles decomposing at 204°. The *platinichloride* forms reddish-yellow needles and decomposes at 169—170°; the *acetyl* derivative separates from dilute alcohol in white needles and the *benzoyl* derivative in white plates; the former melts at 109° and the latter at 144°.

The constitution of the preceding compounds was determined by comparing the above derivatives of the oily nitrothymyl ether with those of 6-nitrothymyl ethyl ether. The *hydrochloride*, *acetyl*, and *benzoyl* derivatives of the latter compound crystallise in white needles and melt respectively at 227—230°, 136°, and 151—152°; the amine reduces platinic chloride and hence the double salt was not obtained.

2:6-Diaminothymyl ethyl ether hydrochloride,



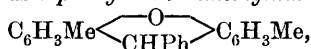
resulting from the complete reduction of the corresponding dinitro-compound, separates from a mixture of concentrated hydrochloric acid, alcohol, and ether as a snow-white powder decomposing at 215°; the *tetra-acetyl* derivative crystallises from dilute alcohol in white flakes melting at 146°.

G. T. M.

**Action of Benzaldehyde on Anisole.** By W. FEUERSTEIN and ANDREAS LIPP (*Ber.*, 1902, 35, 3252—3256).—When a mixture of anisole (2 mols.), benzaldehyde (1 mol.), and glacial acetic acid is added to well-cooled sulphuric acid containing some acetic acid, and after some time is poured on to ice, *phenyldianisylmethane*,  $\text{CHPh}(\text{C}_6\text{H}_4 \cdot \text{OMe})_2$ , separates out. It melts at 100—101° and is sparingly soluble in cold alcohol, but dissolves easily in concentrated sulphuric acid. It has been proved that the benzylidene group is in the *para*-position to the methoxy-groups because the same substance has been obtained by the methylation of 4:4'-dihydroxydiphenylmethane.

With *p*-tolyl methyl ether, a substance of the formula  $\text{CHPh}(\text{C}_6\text{H}_3\text{Me}\cdot\text{OMe})_2$  [ $\text{CHPh}:\text{Me}:\text{OMe}=1:3:5$ ] is formed which melts at  $107-109^\circ$  and is soluble in concentrated sulphuric acid to a violet solution.

The same condensation takes place with *p*-cresol, the *phenol*  $\text{CHPh}(\text{C}_6\text{H}_3\text{Me}\cdot\text{OH})_2$  [ $\text{CHPh}:\text{Me}:\text{OH}=1:3:6$ ] being obtained; this melts at  $158-160^\circ$ , is soluble in the ordinary organic solvents and sulphuric acid, and gives a *diacetyl* derivative which melts at  $121-122^\circ$ . When subjected to distillation, this phenyl-di-*p*-tolylmethane yields 1-phenyl-2:7-dimethylxanthen,



which crystallises in white, silky needles and melts at  $191-191.5^\circ$ ; it is insoluble in alkalis but dissolves in concentrated sulphuric acid giving a green, fluorescent solution.

The condensation with *o*-tolyl methyl ether leads to a substance which melts at  $101-102^\circ$ , the constitution of which is probably  $\text{CHPh}(\text{C}_6\text{H}_3\text{Me}\cdot\text{OMe})_2$ . [ $\text{CH}:\text{Me}:\text{OMe}=1:3:4$ ] I MeO

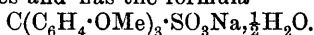
**Dibenzylideneacetone and Triphenylmethane.** By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1902, **35**, 3013—3033. Compare this vol., i, 380).—Trianisylmethane does not, as was at first believed, form coloured salts, and hence this substance, like triphenylmethane, is not halochromic, and the distinction between ammonium and oxonium salts, which was founded on the apparent halochromism of these substances, cannot therefore be maintained.

The properties of triphenylcarbinol in many respects differ from those of both alcohols and acids, and are more closely allied to those of aldehydes or ketones. A close analogy exists between the behaviour of the carbinol to many reagents and that of nitrous acid. The carbinol slowly combines with sodium hydrogen sulphite to form *sodium triphenylmethylsulphonate*,  $\text{CPh}_3\cdot\text{SO}_3\text{Na}\cdot 2\text{H}_2\text{O}$ , which crystallises in large, lustrous plates. The free *acid* crystallises in sparingly soluble needles. When the carbinol is heated with aniline and acetic acid, the anilide, which has been previously prepared from aniline and triphenylbromomethane, is formed. Phenylhydrazine yields with the carbinol a substance which melts at  $108.5^\circ$  and is probably identical with the triphenylmethylazobenzene obtained by Gomberg from triphenylbromomethane. The carbinol also reacts readily with hydroxylamine, yielding a product,  $\text{C}_{33}\text{H}_{32}\text{O}_2\text{N}$ , melting at  $182-184^\circ$ , but the constitution of this substance has not been ascertained. Triphenylcarbinol readily combines with phenol, forming *hydroxytetraphenylmethane*,  $\text{CPh}_3\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , which crystallises in needles or plates and melts at  $282^\circ$ . This substance behaves as a phenol and yields a potassium salt which is readily soluble in alcohol. *Triphenyl-*p*-anisylmethane* is formed from the carbinol and anisole, and crystallises in needles melting at  $194^\circ$ . These reactions with sodium hydrogen sulphite, aniline, and phenol correspond with the reactions of nitrous acid with the same types of compounds, and the analogy is also supported by the ready esterification of the carbinol by alcohols, its

union with sulphuric acid, and the formation of double salts of triphenylchloromethane and metallic chlorides.

The basicity of a number of methoxyl derivatives of benzylideneacetone and triphenylcarbinol was measured by ascertaining how much dilute alcohol was required to hydrolyse, and thus decolorise, solutions of molecular proportions of the various substances in a standard solution of acetic and sulphuric acids. Taking the basicity of dibenzylideneacetone as 1, those of the methoxyl derivatives are as follows: mono-*p*-compound, 3·9; *pp*-compound, 13·5; *oo*-compound, 3·7; *mm*-compound, 1·2. Similarly, taking the basicity of triphenylcarbinol as 1, we have mono-*p*-compound, 6·3; di-*p*-compound, 34; tri-*p*-compound, 286; tri-*o*-compound, 7·6; tri-*m*-compound, 1·7; *oop*-compound, 27·3. In both cases, the effect of the methoxyl group is greatest in the para-position, whilst a greater effect is produced by its introduction into triphenylcarbinol than into dibenzylideneacetone. Comparing the effect of the introduction of the group in the same position into successive rings, it is found that the basicity increases in geometrical ratio, and this leads to the important conclusion that the three phenyl groups of the carbinol have an equal influence on the basicity of the derivatives, so that it becomes improbable that the formation of coloured salts can be referred to the presence of a quinonoid group in which only one phenyl group is concerned.

The increased basicity produced by the introduction of the methoxyl groups is accompanied by an increase in the chemical activity of the hydroxyl group of triphenylcarbinol. Tri-*p*-anisylcarbinol is much more easily reduced than triphenylcarbinol, and also unites with sodium hydrogen sulphite much more rapidly, the reaction taking place at once, whilst in the case of the triphenyl-derivative it requires weeks for its completion. The *sodium* salt produced crystallises in large, colourless plates and has the formula



Tri-*p*-anisylcarbinol is at once acted on by hydrocyanic acid, forming tri-*p*-anisylacetoneitrile, which crystallises in long, rectangular plates and melts at 128·5—129°. Triphenylacetoneitrile has been prepared by heating triphenylchloromethane with mercuric cyanide. Tri-*p*-anisylcarbinol also reacts readily with aniline, forming a blue colouring matter.

These facts further confirm the conclusion that the activity of the hydroxyl group is conditioned, not by any one of the phenyl groups present in the molecule, but by the nature of the whole complex with which the hydroxyl is united.

The following new compounds have been prepared in the course of the work:

*Benzylidene-p-anisylideneacetone* (*p*-methoxydibenzylideneacetone) is obtained by the condensation of benzylideneacetone and *p*-anisaldehyde, and forms nodular crystals melting at 96·5°. Di-*o*-anisylideneacetone, prepared from acetone and *o*-methoxybenzaldehyde, crystallises in bright yellow, rhombic plates and has previously been obtained by Petrenko-Kritschenko. *o*-Methoxybenzaldehyde boils at 114—115° under 12 mm. pressure. Di-*m*-anisylideneacetone is prepared in a similar

manner and purified by conversion into the hydriodide; it crystallises in yellow needles melting at 52—54°. The methoxydibenzylideneacetones behave towards acids in a similar manner to the parent substance.

*Tri-o-anisylcarbinol* is prepared by Grignard's method from iodoanisole and methyl *o*-anisate, and forms colourless, lustrous tablets melting at 181°. *Tri-m-anisylcarbinol* is prepared in a similar manner, and crystallises in tablets melting at 119.5°. *m*-Iodoanisole is prepared by converting *m*-nitroaniline into *m*-nitrophenol, methylating this with methyl sulphate, reducing, diazotising, and finally treating with hydriodic acid. The methyl *m*-anisate is prepared from *m*-hydroxybenzoic acid. *o*o-*Trianisylcarbinol* crystallises in large, lustrous prisms melting at 109—110°, and is prepared from *o*-iodoanisole and methyl *p*-anisate. *Diphenyl-p-anisylcarbinol*, prepared from bromobenzene and methyl *p*-anisate, forms crystalline crusts melting at 58—61°.

*Tri-p-anisylchloromethane* is formed when hydrogen chloride is passed into an ethereal solution of the carbinol, and is a white powder consisting of long prisms; it melts and decomposes at 154—156°, forming a red liquid which probably contains dimethylamine. A. H.

**Auto-oxidation of Pyrogallol.** By CARL D. HARRIES (*Ber.*, 1902, 35, 2954—2959).—When pyrogallol dissolved in barium hydroxide solution is shaken with air, it undergoes oxidation, forming a *hexahydroxydiphenyl*, which probably has the constitution 3 : 4 : 5 : 3' : 4' : 5'. It crystallises from hot water in white needles which begin to decompose when heated to 200°, dissolves in alkali hydroxides giving deep coloured solutions, and reduces Fehling's solution, but yields no quinone when treated with an alcoholic solution of iodine. The *acetyl* derivative crystallises in small, colourless plates and melts at 162—163°.

Alkaline solutions of the substance absorb oxygen, but yield no trace of purpurogallin; it is therefore probable that for the formation of the latter by the auto-oxidation of pyrogallol (Berthelot, *Abstr.*, 1898, i, 645) the presence of pyrogallol as well as the hexahydroxydiphenyl is necessary. R. H. P.

**Halogen Derivatives of the Phloroglucinols. III. Decomposition of Tribromophloroglucinol.** By JOSEF HERZIG and HERMANN KASERER (*Monatsh.*, 1902, 23, 573—581. Compare *Abstr.*, 1886, 232; 1895, i, 343).—Tribromophloroglucinol is hydrolysed by aqueous potassium or barium hydroxide to carbon dioxide and a substance which forms a sparingly soluble barium salt apparently identical with the barium salt of dihydroxydiketocyclopentane described by Hantzsch (*Abstr.*, 1888, 132). G. Y.

**Halogen Derivatives of the Phloroglucinols. IV. Chloro-derivatives of the Ethers of Phloroglucinol.** By HERMANN KASERER (*Monatsh.*, 1902, 23, 582—588. Compare preceding abstract).—When acted on by chlorine in carbon tetrachloride solution, phloroglucinol trimethyl ether forms trichlorophloroglucinol

trimethyl ether, which melts at 130—131° and is identical with Bartolotti's compound (Abstr., 1897, i, 558). It can neither be acetylated nor reduced and is not acted on by boiling water or aqueous alkalis.

Phloroglucinol dimethyl ether yields, on chlorination, a *tetrachloro*-derivative, which crystallises from benzene in large, pale yellow, transparent crystals, melts at 115—117°, darkens on exposure to light, and is soluble in benzene, carbon tetrachloride, and concentrated sulphuric acid, but more sparingly so in light petroleum. It has an odour resembling that of camphor. It is decomposed by alkalis with formation of hypochlorites. The chlorine is only partly eliminated by the action of sodium amalgam or by boiling water. It cannot be acetylated. Reduction with stannous chloride and acetic acid leads to the formation of *trichlorophloroglucinol dimethyl ether*, which crystallises from benzene, melts at 93—95°, is soluble in aqueous alkalis, but is not changed by long boiling with alkalis, and forms an *acetyl* derivative crystallising in large, glistening flakes melting at 58—59° and easily soluble in benzene or light petroleum.

Chlorination of phloroglucinol methyl ether leads to the formation of a *pentachloro*-derivative,  $\text{OMe} \cdot \text{C}_6\text{Cl}_5\text{O}_2$ , which has a yellow colour, melts at 72—74°, is easily soluble in benzene and carbon tetrachloride, but sparingly so in cold light petroleum, and has scarcely any odour. Approximately 4 atoms of chlorine are eliminated by boiling with aqueous potassium hydroxide (compare Abstr., 1900, i, 595). G. Y.

**Alkyl Ethers of the Phloroglucinols. V. Constitution of the Mono- and Di-alkyl Ethers of Methylphloroglucinol.** By JOSEF HERZIG and KARL EISENSTEIN (*Monatsh.*, 1902, 23, 563—572. Compare Abstr., 1901, i, 206).—The mono-methyl and mono-ethyl ethers of methylphloroglucinol, prepared by etherification with alcohol and hydrogen chloride, yield, on further etherification, two methyl-ethyl ethers, which are isomeric and must therefore be alkylated in the *op*-positions. This supports the contention of Bosse (Abstr., 1901, i, 207) that direct etherification of methylphloroglucinol takes place in the first instance in the *p*-position (compare Abstr., 1902, i, 463).

1-Methylphloroglucinol 4-ethyl ether crystallises from benzene in colourless, glistening needles, melts at 136—137°, boils at 195—200° under 13 mm. pressure, and is easily soluble in alcohol or ether. The *diacetyl* derivative crystallises from alcohol in colourless, soft leaflets and melts at 91°.

If, on etherification of the mono-alkyl ethers with alcohol and hydrogen chloride, the reaction be carried too far it results in a non-volatile product, but by stopping it before it has completely reached this stage, a mixture of the mono- and di-alkyl ethers is obtained by distillation. The di-alkyl ethers, which show little tendency to crystallise, are characterised by means of the dibromo- and acetyldibromo-derivatives.

*Dibromomethylphloroglucinol ethyl ether*  $[\text{Me} : \text{OEt} : (\text{OH})_2 : \text{Br}_2 = 1 : 4 : 2 : 6 : 3 : 5]$  crystallises from light petroleum and melts at 115°.

3 : 5-Dibromomethylphloroglucinol 4-methyl ether crystallises from

light petroleum in long needles, melts at  $114^{\circ}$ , and is easily soluble in alcohol or benzene.

3 : 5-Dibromomethylphloroglucinol 2-methyl 4-ethyl ether separates from dilute alcohol in colourless crystals, melts at  $72-74^{\circ}$ , and is easily soluble in alcohol, benzene, or light petroleum. The *acetyl* derivative crystallises from alcohol in long prisms and melts at  $77-78^{\circ}$ . 3 : 5-Dibromomethylphloroglucinol 4-methyl 2-ethyl ether is precipitated from glacial acetic acid, on addition of water, in colourless, hair-like needles and melts at  $84-86^{\circ}$ . The *acetyl* derivative forms monoclinic crystals from alcohol and melts at  $99-101^{\circ}$ . G. Y.

**Reduction of Chrysazin with Hydrogen Iodide.** By H. SCHROESDORFF (*Ber.*, 1902, 35, 2930-2931).—*Dihydroxyanthranol* (*chrysanthranol*),  $\text{CH} \begin{array}{c} \text{C}_6\text{H}_3(\text{OH}) \\ \text{C}_6\text{H}_3(\text{OH}) \end{array} \text{C}\cdot\text{OH}$ , crystallises from light petroleum in minute, lemon-yellow flakes or needles and melts at  $176-177^{\circ}$ . The *triacetyl* derivative crystallises in yellowish needles, melts at  $209-210^{\circ}$ , and is oxidised to diacetylchrysazin. T. M. L.

**Reduction of Quinizarin and Anthrarufin with Hydrogen Iodide.** By B. PLEUS (*Ber.*, 1902, 35, 2923-2930).—In addition to quinizarin hydride, hydroquinizarol, and hydroxyhydroanthranol, which Liebermann and Giesel (*Abstr.*, 1877, ii, 494) obtained as reduction products of quinizarin, 1 : 4-dihydroxyanthranol and hydro- $\alpha$ -anthrol have been obtained.

*Triacetylhydroquinizarol*,  $\text{CH}_2 \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_2(\text{OAc})_2 \end{array} \text{CH}\cdot\text{OAc}$ , prepared by heating hydroquinizarol with sodium acetate and acetic anhydride, forms yellow needles and melts at  $79-80^{\circ}$ ; it is oxidised by chromic acid in acetic acid solution to diacetylquinizarin (*Abstr.*, 1875, 68).

1 : 4-Dihydroxyanthranol,  $\text{CH} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_2(\text{OH})_2 \end{array} \text{CH}\cdot\text{OH}$ , crystallises from alcohol in felted, orange-red needles, melts at  $156^{\circ}$ , and when dissolved in alkali and exposed to air becomes blue through conversion into quinizarin. The *triacetyl* derivative forms small, short, yellow prisms, melts at  $188-189^{\circ}$ , and is oxidised to diacetylquinizarin.

*Diacetylhydroxyhydroanthranol*,  $\text{CH}_2 \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_3(\text{OAc}) \end{array} \text{CH}\cdot\text{OAc}$ , crystallises in yellow needles and melts at  $84-85^{\circ}$ ; this and the mono-*acetyl* compound are oxidised by chromic acid to acetylerthro-oxy-anthraquinone.

*Hydro- $\alpha$ -anthrol*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array} \text{C}_6\text{H}_3(\text{OH})$ , isomeric with Perger's hydroanthranol (*Abstr.*, 1881, 607), crystallises in whitish-yellow flakes, melts at  $94^{\circ}$ , and is not very readily volatile in steam. The *acetyl* derivative forms yellow needles and melts at  $82-85^{\circ}$ .

Two new compounds were also obtained by reducing anthrarufin.

1 : 5-Dihydroxyhydroanthranol,  $\text{CH}_2 \begin{array}{c} \text{C}_6\text{H}_3(\text{OH}) \\ \text{C}_6\text{H}_3(\text{OH}) \end{array} \text{CH}\cdot\text{OH}$ , crystallises from dilute alcohol in golden-yellow needles and melts at  $241^{\circ}$ .

The *triacetyl* derivative crystallises in small, yellowish-white needles, melts at 162—163°, and is oxidised to diacetylanthrurufin.

1 : 5-*Dihydroxyanthranol*,  $\text{CH} \begin{smallmatrix} \text{C}_6\text{H}_3(\text{OH}) \\ \text{C}_6\text{H}_3(\text{OH}) \end{smallmatrix} \text{C}\cdot\text{OH}$ , crystallises from alcohol in glistening, golden flakes and decomposes at 200° without melting. The *triacetyl* derivative crystallises in stout, yellow, monoclinic prisms, melts at 184—185°, and is oxidised to diacetylanthrurufin; it is also formed when the dihydro-compound is dried at 120°, two atoms of hydrogen being eliminated.

*Anthrurufin monoethyl ether*,  $\text{OH}\cdot\text{C}_{14}\text{H}_6\text{O}_2\cdot\text{OEt}$ , crystallises from dilute alcohol in minute, short, canary-yellow needles and melts at 163—164°.

*Acetylanthrurufin monoethyl ether*,  $\text{OAc}\cdot\text{C}_{14}\text{H}_6\text{O}_2\cdot\text{OEt}$ , forms yellowish flakes and melts at 172—173°. The *diethyl* ether crystallises from alcohol in long, yellow, felted, silky needles and melts at 178°.

T. M. L.

**Gradual Synthesis of the Benzene Chain.** By MAURICE DELACRE (*Bull. Acad. roy. Belg.*, 1902, 251—258. Compare Abstr., 1900, i, 603).—The results now published extend and correct those recorded in a previous paper (*Bull. Acad. roy. Belg.*, 1895, 29, 849). When  $\alpha$ -isodypnopinacolin,  $\text{C}_{32}\text{H}_{26}\text{O}$ , is heated to 400° in a vacuum, it rapidly decomposes, furnishing (1) a liquid distillate containing ethylbenzene, allylbenzene, acetophenone, benzaldehyde, and benzoic acid; (2) a semi-solid fraction consisting of triphenylbenzene, *pyrodypnopinacolin*, and an uncrystallisable resin, which, on redistillation under atmospheric pressure, decomposes into ethylbenzene, polymerised allylbenzene, and triphenylbenzene (?).

*Pyrodypnopinacolin*,  $\text{C}_{32}\text{H}_{22}\text{O}$ , crystallises from alcohol in colourless crystals, melts at 166°, and distils between 465° and 475°. Its solubilities in the following media at their boiling points and at the ordinary temperature respectively are: acetic acid, 2.2 and 0.1; alcohol, 2.2 and 0.3; ethyl acetate and acetone, 10 and 1.3 per cent.; it is also more soluble in hot than in cold benzene. With acetic acid, ethyl acetate, benzene, acetone, and acetyl chloride, 2 mols. of the substance combine with 1 mol. of these solvents to form crystalline molecular compounds stable at 100—105°, but which decompose at 150—160°. The acetic acid additive product crystallises in colourless plates, melts at 162°, and is employed as a convenient means of separating *pyrodypnopinacolin* from the bye-products of its preparation. When reduced in alcoholic solution by means of sodium amalgam, or when treated with zinc ethyl, *pyrodypnopinacol alcohol*,  $\text{C}_{32}\text{H}_{24}\text{O}$ , is produced. The latter forms characteristically grouped, colourless needles, melts at 156° and distils at 310—328° under 15 mm., but when heated under atmospheric pressure (or in a vacuum if impure), it decomposes into benzaldehyde and a solid hydrocarbon,  $\text{C}_{25}\text{H}_{18}$  (?). It dissolves in alcohol, acetic acid, or benzene, but is insoluble in light petroleum.

*Pyrodypnopinalcolene*,  $\text{C}_{32}\text{H}_{22}$ , is produced when *pyrodypnopinacolin* is treated with hydriodic acid (with concentrated acid, triphenylbenzene is also formed) or when *pyrodypnopinacolyl alcohol* is dissolved in

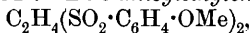


acetyl chloride or acted on by phosphorus pentachloride. It crystallises in silky needles, which melt at  $136^{\circ}$ , or in large, transparent crystals, which melt at  $154\text{--}156^{\circ}$ , and boils at  $330\text{--}333^{\circ}$  under 15 mm. pressure. Its solubilities in the following media at their boiling points and at the ordinary temperature respectively are, alcohol, 1 and 0.11; acetic acid, 13.7 and 1.6; benzene, 153.8 and 35.6 per cent. When heated in alcoholic solution with sodium, or when oxidised by nitric acid, it is converted into *dehydropyrodypnopinacolyl alcohol*,  $C_{32}H_{22}O$ . This forms colourless crystals, melts at  $203.5^{\circ}$  and distils in a vacuum at  $300\text{--}320^{\circ}$  with slight decomposition. Its solubilities in the following media, at their boiling points and at the ordinary temperature respectively are: alcohol, 0.74 and 0.15; acetic acid, 4.16 and 1.13; benzene, 20.8 and 2.8 per cent. With the latter, an additive compound appears to be formed. When heated with hydriodic acid, pyrodypnopinalcolene is re-obtained. With acetyl chloride, *dehydropyrodypnopinacolyl acetate*,  $C_{34}H_{24}O_2$ , forming colourless crystals which melt at  $200^{\circ}$ , is produced. This dissolves readily in benzene, less so in acetic acid and alcohol. On saponification, the alcohol is not regenerated. When repeatedly recrystallised from acetic acid, it appears to be converted into the pyrodypnopinalcolene already described.

The author supposes that  $\alpha$ -isodypnopinacolin may be represented by the formula  $C_8H_6OPh_4$ , in which case pyrodypnopinacolin might be written  $C_8H_2OPh_4$ , or  $C_8H_6OPh_2(C_6H_4)_2$ , or  $C_8H_4O(C_6H_4)_4$ , the second or third expression being the more probable. T. A. H.

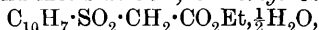
**Aryl sulphonated Alcohols and Acids.** By JULIUS TROEGER and CHR. BUDDE (*J. pr. Chem.*, 1902, [ii], 66, 130—152. Compare Abstr., 1897, i, 223).—*Di-m-xylylethylenedisulphone*,  $C_2H_4(SO_2 \cdot C_8H_9)_2$ , formed by the action of an alcoholic solution of ethylene dibromide on sodium *m*-xylenesulphinate, prepared by Gattermann's method from 1:3:4-xylidine, crystallises from alcohol in rosettes of needles, melts at  $163^{\circ}$ , is easily soluble in hot alcohol, more sparingly so in ether. When boiled with 30 per cent. potassium hydroxide solution, it yields *m*-xylenesulphinic acid and a semi-solid oil which is a mixture of *m*-xylylsulphonethylic alcohol,  $C_8H_9 \cdot SO_2 \cdot CH_2 \cdot CH_2 \cdot OH$ , and its ether,  $(C_8H_9 \cdot SO_2 \cdot C_2H_4)_2O$ . The proportion of ether is increased if the hydrolysis be carried out under pressure. A preparation of di-*m*-xylylethylenedisulphone, obtained from a sulphinic acid prepared by reduction of *m*-xylenesulphonic chloride with zinc dust, melted at  $146^{\circ}$  and on hydrolysis yielded a xylenesulphinic acid melting at  $55^{\circ}$  and an oil consisting apparently of only xylylsulphonethylic alcohol. The following disulphones were obtained by prolonged warming of ethylene dibromide with the corresponding sodium sulphinate in alcoholic solution. *Di-p-xylylethylenedisulphone*, which crystallises from alcohol in needles, melts at  $174^{\circ}$  and on hydrolysis yields the sulphinic acid and *p*-xylylsulphonethylic alcohol,  $C_8H_9 \cdot SO_2 \cdot C_2H_4 \cdot OH$ , as a light coloured oil. *Di-ψ-cumylethylenedisulphone*,  $C_2H_4(SO_2 \cdot C_9H_{11})_2$ , which separates from alcohol in needles melting at  $241^{\circ}$  and, on hydrolysis with potassium hydroxide solution at  $150^{\circ}$ , yielding a mixture of  $\psi$ -cumylsulphonethylic alcohol and its ether,  $(C_9H_{11} \cdot SO_2 \cdot C_2H_4)_2O$ . *Di-α-naphthylethylenedisulphone*,  $C_2H_4(SO_2 \cdot C_{10}H_7)_2$ , which crystallises from alcohol in

needles, melts at  $194^{\circ}$  and on hydrolysis yields *α*-naphthylsulphonethylic alcohol,  $C_{10}H_7 \cdot SO_2 \cdot CH_2 \cdot CH_2 \cdot OH$ , which is an oil. *Di-β-naphthylethylenedisulphone*, which crystallises from alcohol in needles, melts at  $258^{\circ}$  and yields *β*-naphthylsulphonethylic alcohol as a white, crystalline powder melting at  $88-90^{\circ}$ . *Di-p-chlorophenylethylenedisulphone*,  $C_2H_4(SO_2 \cdot C_6H_4Cl)_2$ , crystallising from alcohol in microscopic needles which melt at  $255^{\circ}$  and on hydrolysis yielding the sulphinic acid and *p*-chlorophenylsulphonethylic alcohol,  $C_6H_4Cl \cdot SO_2 \cdot C_2H_4 \cdot OH$ , as a thick, brown oil. *Di-p-bromophenylethylenedisulphone*, which melts at  $261^{\circ}$  and yields *p*-bromophenylsulphonethylic alcohol, which forms a crystalline mass and melts at  $50-52^{\circ}$ . *Di-o-anisylethylenedisulphone*,



which forms needles, melts at  $175^{\circ}$ , and yields *o*-anisylsulphonethylic alcohol,  $OMe \cdot C_6H_4 \cdot SO_2 \cdot C_2H_4 \cdot OH$ , which forms a crystalline mass and melts at  $82^{\circ}$ . These arylsulphonethylic alcohols are easily soluble in alcohol or ether, more sparingly so in water.

The following arylsulphonacetic acids have been prepared by the action of ethyl chloroacetate on the corresponding sodium sulphinate and hydrolysis of the ester so obtained. *m*-Xylylsulphonacetic acid,  $C_8H_9 \cdot SO_2 \cdot CH_2 \cdot CO_2H$ , is crystalline and melts at  $56^{\circ}$ . *p*-Xylylsulphonacetic acid is an oil. *ψ*-Cumylsulphonacetic acid,  $C_9H_{11} \cdot SO_2 \cdot CH_2 \cdot CO_2H$ , forms granular crystals and melts at  $62^{\circ}$ . *α*-Naphthylsulphonacetic acid,  $C_{10}H_7 \cdot SO_2 \cdot CH_2 \cdot CO_2H$ , crystallises in glistening leaflets and melts at  $168^{\circ}$ . *β*-Naphthylsulphonacetic acid,  $C_{12}H_{10}O_4S \cdot H_2O$ , forms a white, crystalline powder and melts at  $90^{\circ}$ ; the *ethyl* ester,



melts at  $82^{\circ}$ , the *sodium* salt crystallises from alcohol in white needles. *p*-Chlorophenylsulphonacetic acid,  $C_6H_4Cl \cdot SO_2 \cdot CH_2 \cdot CO_2H$ , crystallises in small, glistening leaflets and melts at  $122^{\circ}$ , the *ethyl* ester is an oil. *p*-Bromophenylsulphonacetic acid,  $C_6H_4Br \cdot SO_2 \cdot CH_2 \cdot CO_2H$ , crystallises in needles and melts at  $143^{\circ}$ , the *ethyl* ester,  $C_8H_6O_4SBrEt \cdot H_2O$ , crystallises in silky needles and melts at  $52^{\circ}$ . *o*-Anisylsulphonacetic acid,  $OMe \cdot C_6H_4 \cdot SO_2 \cdot CH_2 \cdot CO_2H$ , crystallises in needles and melts at  $138^{\circ}$ , the *ethyl* ester is obtained as an oil which slowly solidifies.

The following alkylsulphones,  $C_6H_5Me_2 \cdot SO_2R$ , have been obtained by the action of alkyl haloids on sodium *m*-xylenesulphinate. *m*-Xylylmethylsulphone forms crystals from alcohol and melts at  $55^{\circ}$ . *m*-Xylylethylsulphone solidifies on standing and melts at  $53^{\circ}$ . *m*-Xylyl-*n*-propylsulphone crystallises from dilute alcohol in needles and melts at  $68-69^{\circ}$ . *m*-Xylyl-isopropyl-, *butyl*-, *amyl*-, and *cetyl*-sulphones are oily substances and could not be obtained free from halogen. *m*-Xylyldiallylsulphone is obtained sometimes crystalline, sometimes as an oil; the compound last mentioned combines with bromine, forming a crystalline dibromide which melts at  $56-57^{\circ}$ .

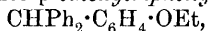
*o*-Anisylmethylsulphone,  $OMe \cdot C_6H_4 \cdot SO_2Me$ , crystallises from alcohol and melts at  $84^{\circ}$ .

G. Y.

*p*-Hydroxytriphenylcarbinol. II. By AUGUSTIN BISTRZYCKI and CARL HERBST (*Ber.*, 1902, 35, 3133-3141. Compare Abstr., 1901, i, 701).—Crude, orange-coloured *p*-hydroxytriphenylcarbinol may be obtained perfectly colourless by repeated crystallisation from acetic

acid and water, or by conversion into its acetyl derivative and subsequent hydrolysis with alkali and crystallisation from acetic acid. The *sodium* derivative,  $\text{ONa} \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2 \cdot \text{OH}$ , forms colourless plates.

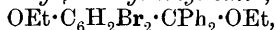
*p*-Ethoxytriphenylcarbinyl ethyl ether,  $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2 \cdot \text{OEt}$ , crystallises from aqueous alcohol in colourless, microscopic plates melting at  $87^\circ$ . It may be obtained by the action of alkali and ethyl iodide or of hydrogen chloride and alcohol on the hydroxycarbinol. The *methyl* ether,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2 \cdot \text{OMe}$ , melts at  $74^\circ$  and is readily soluble in most organic solvents with the exception of light petroleum. When boiled with glacial acetic acid, acetyl chloride, or acetic anhydride, the ethyl ether is converted into *p*-ethoxytriphenylmethane,



which crystallises in well-formed, doubly refractive plates melting at  $70$ – $71^\circ$ . The methyl ether, when similarly treated, yields *p*-methoxytriphenylcarbinol melting at  $84^\circ$ .

*p*-Hydroxytriphenylmethane, obtained by the reduction of the corresponding carbinol with zinc and acetic acid, crystallises in microscopic plates melting at  $110^\circ$ . The *methyl* ether melts at  $61^\circ$  and the *acetyl* derivative at  $84^\circ$ .

*Dibromo-p*-ethoxytriphenylcarbinyl ethyl ether,



obtained by alkylating the dibromohydroxycarbinol (Abstr., 1901, i, 701), crystallises in well-formed plates melting at  $105^\circ$ . The *dimethyl* compound crystallises in microscopic prisms, melts at  $98^\circ$ , and when boiled with acetic anhydride yields an *ether*,  $\text{O}(\text{CPh}_2 \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{OMe})_2$ , melting at  $133^\circ$ . The diethyl compound under similar treatment yields *dibromo-p*-ethoxytriphenylmethane melting at  $132^\circ$ .

*Dibromo-p*-hydroxytriphenylmethane, obtained by the reduction of the carbinol, crystallises in small prisms melting at  $131^\circ$  and yields an *acetyl* derivative melting at  $112$ – $113^\circ$ . Most of the ethers described do not give correct results for ethoxy- or methoxy-estimations by the Zeisel method.

J. J. S.

**Constitution of a New *o*-Chlorodinitrobenzoic Acid and of *o*-Chloro-*m*-nitrobenzoic Acid.** By ATTILIO PURGOTTI and A. CONTARDI (*Gazzetta*, 1902, 32, i, 526–537).—The authors have determined the constitutions of the two following acids:

The dinitro-*o*-chlorobenzoic acid described by Kalle (D.R.-P. 106510) and melting at  $199$ – $200^\circ$ . This acid is best prepared by heating at  $130$ – $140^\circ$  a mixture of *o*-chlorobenzoic acid, sulphuric acid, and fuming nitric acid in suitable proportions. It boils at  $240$ – $241^\circ$  and at  $253^\circ$  decomposes, and for the most part explodes; it is slightly soluble in water, but almost insoluble in the other solvents. Since when nitrated in the cold with a mixture of sulphuric and nitric acids, *o*-chlorobenzoic acid yields the nitro-*o*-chlorobenzoic acid melting at  $165^\circ$  described by Hübner (Abstr., 1884, 599), and this at higher temperatures gives, with the same nitrating mixture, Kalle's acid, the latter, as well as Hübner's acid, must have a nitro-group in the 3- or 5-position. Further, the dinitro-acid gives an almost theoretical yield of the methyl ester in presence of hydrogen chloride, and as position 2 is occupied by chlorine, position 6 must, according to

Victor Meyer's rule, be free. When heated with excess of ammonia solution, the acid yields the dinitroaminobenzoic acid,  $[\text{NH}_2 : 2\text{NO}_2 = 2 : 3 : 5]$ , which, with dilute sodium hydroxide solution, gives the corresponding dinitrosalicylic acid, hence Kalle's acid has the constitution  $[\text{Cl} : \text{NO}_2 : \text{NO}_2 = 2 : 3 : 5]$ . When boiled with excess of barium hydroxide solution, it yields *o-p*-dinitrophenol. The acid may also be prepared synthetically by heating *m*-dinitrosalicylic acid with phosphorus pentachloride.

The *o*-chloro-*m*-nitrobenzoic acid described by Hübner (*loc. cit.*), when boiled for some time with excess of concentrated potassium hydroxide solution, yields the nitrosalicylic acid  $[\text{CO}_2\text{H} : \text{OH} : \text{NO}_2 = 1 : 2 : 5]$ . The constitution of the acid must hence be  $\text{CO}_2\text{H} : \text{Cl} : \text{NO}_2 = 1 : 2 : 5$ .  
T. H. P.

**Derivatives of *o*-Chlorodi-*m*-dinitrobenzoic Acid. II.** By ARTILIO PURGOTTI and A. CONTARDI (*Gazzetta*, 1902, 32, i, 573—579. Compare preceding abstract).—The following derivatives of *o*-chlorodi-*m*-dinitrobenzoic acid have been examined :

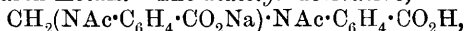
The *silver* salt, crystallising in thin, white needles ; the *sodium* salt, forming yellow scales ; the *potassium*, *ammonium*, *barium*, *calcium*, *copper*, *nickel*, *manganese*, *cobalt*, and *lead* salts were also prepared. The *methyl* ester forms small, acicular crystals which have a pungent odour, melt at  $87^\circ$ , and dissolve in methyl alcohol, and, to a less extent, in ether, water, or benzene. The *ethyl* ester forms plates melting at  $54^\circ$ , and is soluble in alcohol or ether. When heated with three molecular proportions of aniline, the acid reacts according to the equation  $\text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)_2 \cdot \text{CO}_2\text{H} + 3\text{NH}_2\text{Ph} = \text{NHPh} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{CO}_2\text{H} \cdot \text{NH}_2\text{Ph} + \text{NH}_2\text{Ph} \cdot \text{HCl}$ . The *aniline o-phenylamino-di-m-nitrobenzoate* thus obtained crystallises from water in slender, shining, red needles which begin to decompose at  $141^\circ$  and at  $253^\circ$  melt and carbonise. The free *acid* forms orange-yellow needles which melt at  $215^\circ$  and are readily soluble in alcohol or benzene ; the *potassium* salt forms bright red, shining leaflets.

The action of hydrazine hydrate on *o*-chlorodi-*m*-dinitrobenzoic acid yields an internal *anhydride* of the constitution  $\text{C}_6\text{H}_2(\text{NO}_2)_2 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{NH}$ , which separates from water in yellow prisms decomposing without melting at  $185\text{--}215^\circ$ .  
T. H. P.

**Methylantranilic Acid.** By GUSTAV SCHULTZ and J. FLACHS-LÄNDER (*Chem. Centr.*, 1902, ii, 448 ; from *Zeit. Farb. Textilchem.*, 1902, 1, 353—354).—*Methylantranilic acid*,  $\text{NHMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , prepared by the action of methyl iodide on anthranilic acid, crystallises from alcohol in leaflets which show a greenish lustre, melts at  $177^\circ$ , and is soluble in alcohol or ether, forming solutions with a blue fluorescence ; it is almost insoluble in water. When the acid is heated above its melting point, it decomposes, forming methylaniline, and when melted with alkali it yields indigo. The *hydrochloride*,  $\text{C}_8\text{H}_9\text{O}_2\text{N} \cdot \text{HCl}$ , crystallises in needles, melts at  $141^\circ$ , and is readily soluble in alcohol, but only slightly so in water or ether. *Acetylmethylantranilic acid*,  $\text{NAcMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , crystallises in needles, melts at  $192^\circ$ , and is readily

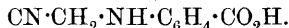
soluble in hot water or alcohol, but only sparingly so in ether. *Methyl methylantranilate*,  $\text{NHMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ , is liquid, has the odour of jasmine, and boils at  $129^\circ$  under 13 mm. pressure. *Nitrosomethyl-anthranilic acid*,  $\text{NO}\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , crystallises from benzene in reddish-yellow crystals, has not a definite melting point, and is readily soluble in alcohol, ether, or hot water. The *hydrochloride* of *p*-nitroso-methylantranilic acid,  $\text{NHMe}\cdot\text{C}_6\text{H}_3(\text{NO})\cdot\text{CO}_2\text{H}\cdot\text{HCl}$ , dissolves in water or alcohol forming a green solution, and on heating forms *p*-nitroso-methylaniline with elimination of carbon dioxide. E. W. W.

**Action of Formaldehyde on Anthranilic Acid.** By GUSTAV HELLER and GEORG FIESSELMANN (*Annalen*, 1902, 324, 118—137. Compare Abstr., 1901, i, 710).—*Methylenebisanthranilic acid*,  $\text{CH}_2(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$ , prepared by adding 40 per cent. formaldehyde solution to an alcoholic solution of anthranilic acid, separates from acetone as a white, crystalline powder which becomes yellow at  $150^\circ$  and decomposes at  $158^\circ$ ; it also crystallises from ethyl benzoate. It dissolves in alcohol but does not crystallise from this solvent, and it undergoes transformation when treated with glacial acetic acid. The ammoniacal solution of the compound yields precipitates with solutions of the salts of the heavy metals, but not with those of magnesium and the alkaline earth metals. The *diacetyl* derivative,

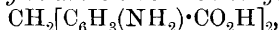


produced by heating the preceding acid with acetic anhydride and anhydrous sodium acetate, is a colourless, crystalline powder decomposing at  $284^\circ$ ; it is readily hydrolysed by dilute hydrochloric acid into formaldehyde and acetylanthranilic acid.

The methylene compound, when dissolved in pyridine and treated with benzoyl chloride, loses its methylene group and yields benzoylanthranil. Potassium cyanide decomposes the methylene compound into anthranilic acid and anthranilinoacetonitrile,



4 : 4'-Diaminodiphenylmethane-3 : 3'-dicarboxylic acid,



obtained by heating the methylenebisanthranilic acid with dilute hydrochloric acid, is isolated in the form of its *hydrochloride*,  $\text{C}_{15}\text{H}_{16}\text{O}_4\text{N}_2\text{Cl}_2$ , by adding to the product excess of the concentrated reagent. The acid set free by the hydrolytic dissociation of its hydrochloride in aqueous solution crystallises in needles and decomposes at  $254^\circ$ . When heated with dilute hydrochloric acid at  $200^\circ$ , it readily loses carbon dioxide, yielding 4 : 4'-diaminodiphenylmethane. A solution of the neutral sodium salt of this acid yields a crystalline *calcium* salt,  $\text{C}_{15}\text{H}_{12}\text{O}_4\text{N}_2\text{Ca}$ , when treated with calcium chloride; similar insoluble salts are obtained by the interaction of solutions of other metallic salts.

The *ethyl* ester,  $\text{CH}_2[\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{CO}_2\text{Et}]_2$ , produced by heating the hydrochloride with ethyl alcohol and concentrated sulphuric acid, separates in aggregates of slender needles melting at  $109^\circ$ ; the methyl ester, prepared in a similar manner, has already been described (Abstr., 1901, i, 470).

The *diacetyl* derivative,  $\text{CH}_2[\text{C}_6\text{H}_3(\text{NHAc})\cdot\text{CO}_2\text{H}]_2$ , prepared by Pin-

now's method, is insoluble in the ordinary organic solvents excepting glacial acetic acid, but dissolves in solutions of sodium acetate or alkali hydroxides and carbonates; it decomposes at 259—261°. The *dibenzoyl* derivative, produced by the Schotten-Baumann reaction, crystallises from glacial acetic acid in needles decomposing at 268°; it also dissolves in pyridine or in hot acetone or alcohol. This compound forms soluble alkali salts which are precipitated by excess of the alkali hydroxide or carbonate.

*Dibenzoyldianthranilylmethane*,  $\text{CH}_2\left(\text{C}_6\text{H}_3\left\langle\begin{smallmatrix} \text{NBz} \\ \text{CO} \end{smallmatrix}\right.\right)_2$ , resulting from the action of benzoyl chloride on the diphenylmethane derivative in pyridine solution, crystallises from this solvent in needles, or from toluene in sheaf-like aggregates, and melts at 287—288°; it is insoluble in dilute solutions of the alkali hydroxides, but when heated with excess of these reagents becomes converted into the alkali salt of the preceding benzoyl derivative.

The action of benzoyl chloride on anthranilic acid in pyridine solution also leads to the formation of the inner anhydride, which in this case is benzoylanthranil.

G. T. M.

**Substituted Aminobenzyl Cyanides and Iminobenzoyl Cyanides.** By FRANZ SACHS and MAX GOLDMANN (*Ber.*, 1902, 35, 3319—3361).—A continuation of previous work (*Abstr.*, 1899, i, 884, and 1901, i, 272). The general methods of preparing substituted aminobenzyl cyanides,  $\text{CN}\cdot\text{CHPh}\cdot\text{NHR}$ , and their oxidation products, the iminobenzoyl cyanides,  $\text{CN}\cdot\text{CPh}\cdot\text{NR}$ , are described in detail.

**I. Derivatives of Primary Monoamines.**—Anilinobenzyl cyanide (*loc. cit.*) yields a *nitroso*-derivative,  $\text{CN}\cdot\text{CHPh}\cdot\text{NPh}\cdot\text{NO}$ , which crystallises in clusters of needles, melts at 55°, and when treated with benzaldehyde, benzotrichloride, and zinc chloride, forms derivatives of triphenylmethane. *p*-Toluidinobenzyl cyanide crystallises from light petroleum in prisms melting at 110°, and the *m*-compound in transparent leaflets melting at 97°. *m*-Tolyliminobenzoyl cyanide crystallises in yellow needles melting at 43°. *a*-Naphthylaminobenzyl cyanide crystallises in leaflets melting at 113°, and the corresponding iminobenzoyl cyanide in lemon-coloured needles melting at 103°. *β*-Naphthylaminobenzyl cyanide crystallises in colourless clusters of laminæ melting at 119—120°, and the iminobenzoyl cyanide in small, yellow rods melting at 124°. *p*-Bromoanilinobenzyl cyanide crystallises in white leaflets melting at 99°, and the corresponding oxidation product in yellow, felted needles melting at 118°. *o*-Carboxyanilinobenzyl cyanide and the corresponding acid (this vol., i, 467) are completely destroyed by permanganate.

The potassium salt of *p*-sulphanilinobenzyl cyanide was obtained as a crystalline, white powder, and the potassium salt of *p*-sulphophenyliminobenzoyl cyanide as lustrous, long, pale yellow prisms. *m*-Nitroanilinobenzyl cyanide crystallises in fine, yellow needles melting at 109°, yields a *nitrosoamine* which crystallises in yellowish, compact prisms melting and decomposing at 90—91°, and, when hydrolysed, the corresponding acid, which crystallises in slender, yellow needles, melts

at  $151^{\circ}$ , and forms a *nitrosoamine* melting at  $156^{\circ}$ ; *m*-nitrophenyliminobenzoyl cyanide forms long, yellow, feathery, silky crystals melting at  $120^{\circ}$ . *p*-Nitroanilinobenzyl cyanide crystallises in bright yellow, rhombic laminæ melting at  $128^{\circ}$ , and the *azomethine* in long, lemon-coloured prisms melting at  $128^{\circ}$ .

*II. Derivatives of Diamines and Aminophenols.*—*p*-Phenylenediaminobenzoyl cyanide,  $C_6H_4(NH \cdot CHPh \cdot CN)_2$ , crystallises in microscopic prisms melting at  $163^{\circ}$ , and its oxidation product in orange-yellow prisms melting at  $233^{\circ}$ . The condensation product of acetyl-*p*-phenylenediamine and mandelonitrile crystallises in quadratic leaflets melting at  $180^{\circ}$ , and its oxidation product in orange-red needles melting at  $146^{\circ}$ . The corresponding compounds from benzoyl-*m*-phenylenediamine and mandelonitrile were also prepared; phenyl- $\mu$ -cyanazomethine-3-benzoylaminophenyl,  $CN \cdot CPh \cdot N \cdot C_6H_3 \cdot NH \cdot CPh$ , crystallises in yellow needles melting at  $139^{\circ}$ . The hydrolysis of *p*-dimethylaminophenylaminobenzyl cyanide yields the corresponding *amide*, which crystallises in straw-coloured needles, melts at  $154$ — $155^{\circ}$ , is readily oxidised to the corresponding *azomethine* which crystallises in orange-yellow needles, and melts and decomposes at  $170^{\circ}$ , and when hydrolysed yields benzylidene-*p*-aminodimethylaniline. *p*-Hydroxyanilinobenzyl cyanide crystallises from alcohol in white leaflets, but is very unstable, as it readily evolves hydrogen cyanide and yields benzylideneaminophenol. *p*-Ethoxyanilinobenzyl cyanide crystallises in yellow, rhombic laminæ, melts at  $85^{\circ}$ , and when oxidised yields phenyl- $\mu$ -cyanazomethine-4-hydroxyphenyl.

Benzidine condenses with benzylidenecyanohydrin forming *bis- $\alpha$ -cyano-benzyl-*p*-diaminodiphenyl*, which crystallises in octahedra, melts at  $201$ — $202^{\circ}$ , and when oxidised yields the corresponding *azomethine*, which crystallises in yellow needles and melts at  $252^{\circ}$ .

*III. Derivatives of Aminoazo-compounds.*—*p*-Azophenyl- $\alpha$ -cyanobenzylaniline crystallises in bronze-coloured needles, melts at  $116^{\circ}$ , and forms a *platinichloride*, which crystallises in large, red laminæ with a metallic lustre; the corresponding *azomethine* forms an orange-red, crystalline powder and melts at  $138$ — $139^{\circ}$ . The analogous compound from benzeneazo- $\beta$ -naphthylamine crystallises in red laminæ melting at  $142^{\circ}$ , and the *azomethine* in small needles which decompose at  $198^{\circ}$ .

Benzylidenecyanohydrin and benzeneazo- $\alpha$ -naphthylamine condense, forming a colourless compound,  $C_{23}H_{17}N_3$ , of undetermined constitution, which melts at  $198^{\circ}$  and is probably identical with the compound obtained by Goldschmidt and Rozell (*Abstr.*, 1890, i, 614) by the condensation of benzaldehyde and benzeneazo- $\alpha$ -naphthylamine.

*IV. Derivatives of Secondary Monoamines.*—Methylanilinobenzyl cyanide crystallises in compact, white prisms melting at  $67^{\circ}$ , forms an unstable *nitrosoamine* which crystallises in yellowish-green plates decomposing at  $80$ — $83^{\circ}$ , and a *mononitro*-derivative which melts at  $127^{\circ}$ .

The *azomethine*,  $NO_2 \cdot C_6H_4 \cdot C(CN) : N \cdot C_6H_4 \cdot NMe \cdot CHPh \cdot CN$ , is a dark red, crystalline powder which melts and decomposes at  $174^{\circ}$ . The *amide*, obtained by the hydrolysis of methylanilinobenzyl cyanide, crystallises in white needles melting at  $133^{\circ}$  and forms a more stable *nitroso*-derivative, which decomposes at  $185$ — $186^{\circ}$ , a *p*-nitro-derivative,

which melts and decomposes at  $210^{\circ}$ , and a *dinitro*-derivative, which decomposes at  $170$ — $172^{\circ}$ . The *azomethine*,

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{CN}) : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{CHPh} \cdot \text{CO} \cdot \text{NH}_2$ , crystallises in small, dark purple pyramids, sinters at  $182^{\circ}$ , and decomposes at  $200^{\circ}$ .

*Ethylanilinobenzyl cyanide* is an oil which yields a crystalline *amide* melting at  $135^{\circ}$ . *Benzylaminobenzyl cyanide* crystallises in white needles melting at  $134^{\circ}$ . The triphenylmethane derivatives, nitrosoamines, and condensation products with nitrobenzyl cyanide of these two nitriles and their amides were also investigated. Attempts to obtain the corresponding acids from these amides were unsuccessful.

R. H. P.

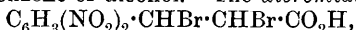
**Dibromocinnamic Acids and Dihalogen-indones.** By A. GLAWE (*Ber.*, 1902, 35, 2936—2940).—By the action of concentrated sulphuric acid,  $\beta$ -dibromocinnamic acid is converted, after twenty hours, into dibromodiketohydrindene,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{CBr}_2$ , the dibromoindone,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CBr} \end{smallmatrix} \text{CBr}$ , which is first formed being also converted into the same compound.  $\alpha$ -Dibromocinnamic acid behaves in a similar manner, but only when heated to  $110^{\circ}$ . Dichloroindone does not behave in this way.

*Bromodimethoxyhydrindone*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{OH}) \\ \diagup \quad \diagdown \\ \text{C}(\text{OMe})_2 \end{smallmatrix} \text{CBr}$ , prepared by the action of sodium methoxide on dibromoindone, crystallises from dilute methyl alcohol and melts at  $79^{\circ}$ . The corresponding *chloro*-compound melts at  $85^{\circ}$ .

*Bromodiethoxyhydrindone*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{OH}) \\ \diagup \quad \diagdown \\ \text{C}(\text{OEt})_2 \end{smallmatrix} \text{CBr}$ , separates from dilute alcohol as a white, crystalline powder and melts at  $60$ — $61^{\circ}$ . *Chloroethoxyindone*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{OEt}) \end{smallmatrix} \text{CCl}$ , which results from the action of sodium ethoxide on dichloroindone, crystallises from alcohol in yellow needles and melts at  $69$ — $70^{\circ}$ ; chlorodiethoxyhydrindone appears also to be produced.

T. M. L.

**Dinitrocinnamic Acid.** By PAUL FRIEDLÄNDER and R. FRITSCH (*Monatsh.*, 1902, 23, 534—542. Compare *Abstr.*, 1885, 1137).—*o-p*-Dinitrocinnamic acid, prepared by Perkin's reaction from *op*-dinitrobenzaldehyde, crystallises from water or toluene in light yellow needles, melts at  $179^{\circ}$ , is easily soluble in hot water, benzene, alcohol, or glacial acetic acid, and dissolves on warming in sodium acetate solution. The *sodium*, *potassium*, *ammonium*, *barium*, *zinc*, *silver*, *lead*, *iron*, *manganese*, and *cobalt* salts are described; they all explode when heated. The *ethyl* ester crystallises from dilute alcohol in yellow needles, melts at  $94^{\circ}$ , is insoluble in water or light petroleum, and easily soluble in benzene or alcohol. The *dibromide*,



formed by combination of bromine and *op*-dinitrocinnamic acid, crystallises from dilute alcohol in large, yellow needles, melts at  $212^{\circ}$ , is easily soluble in alcohol, ethyl acetate, or glacial acetic acid, is par-



tially decomposed by hot water, and on addition of sodium hydroxide to the cold alcoholic solution immediately yields sodium bromide.

Reduction of *op*-dinitrocinnamic acid with ferrous sulphate and ammonia leads to the formation of a reddish-brown, amorphous precipitate. On reduction with stannous chloride and hydrochloric acid, aminocarbostyryl is formed, which crystallises from dilute alcohol in long, colourless needles, becomes gradually red in colour, melts above  $250^{\circ}$ , is easily soluble in alcohol, glacial acetic acid, or hot water, less readily so in cold water, is dibasic, and forms crystalline salts.

*op*-Dinitrobenzylidenemalononic acid,  $C_6H_3(NO_2)_2 \cdot CH:C(CO_2H)_2$ , formed by the action of dinitrobenzaldehyde on malonic acid in presence of acetic acid, crystallises from water in colourless, delicate crystals containing  $1H_2O$ , melts at  $49^{\circ}$ ; the anhydrous acid melts at  $167^{\circ}$ , but evolves carbon dioxide slowly at  $150^{\circ}$ . The *barium* and *silver* salts are described. The *diethyl* ester, formed from dinitrobenzaldehyde and diethyl malonate in presence of piperidine, crystallises from benzene in colourless needles and melts at  $97^{\circ}$ . G. Y.

**Synthesis of Polycyclic Hydrocarbons.** By MAURICE DELACRE (*Bull. Soc. Chim.*, 1902, [iii], 27, 875—882).—By the action of ethyl trichloroacetate on benzene in presence of aluminium chloride, the author has obtained fluorene-carboxylic acid, which is sparingly soluble in the ordinary solvents; the solutions are generally fluorescent. If slowly heated, the acid melts at  $209$ — $210^{\circ}$ , but if it is first plunged into a bath heated to  $180^{\circ}$  it does not melt until  $216$ — $217^{\circ}$ . It readily sublimes at  $200^{\circ}$  and undergoes decomposition at  $280$ — $290^{\circ}$ , carbon dioxide being evolved and fluorene formed. The fluorene so obtained crystallises from alcohol in dazzlingly white, pearly scales, melts at  $115^{\circ}$ , and is quite unaltered by light. The acid obtained in this manner agrees in properties with that obtained by Friedländer (*Abstr.*, 1877, 492), but the ethyl ester obtained from it is quite different, forming glassy crystals which melt at  $60^{\circ}$  and are very soluble in alcohol. The above synthesis appears to be a general one, and applicable to the formation of substituted fluorenes. A. F.

**Affinities of the Halogenated Hydroxybenzoic Acids in Relation to their Constitution.** By ANGELO COPPADORO (*Gazzetta*, 1902, 32, i, 537—572).—The author has measured the affinities of a large number of derivatives of benzoic acid containing at the same time one or more halogens and hydroxyl groups. The entry of a hydroxyl group into benzoic acid in either the ortho- or meta-position produces an increase in the affinity constant, whilst in the para-position a diminution takes place; when other hydroxyl groups now enter the molecule, they produce in some cases an increase, in others a decrease, in the affinity constant. Ostwald's method was used in the author's measurements, the temperature employed being  $25^{\circ}$ . The melting points of the acids examined are given in brackets.

5-Chlorosalicylic acid ( $172^{\circ}$ ) is 1.9 times as strong as salicylic acid; 3:5-dichlorosalicylic acid ( $219.5^{\circ}$ ), 2.4 times as strong as 5-chlorosalicylic acid; 5-chloro-2-ethoxybenzoic acid ( $118^{\circ}$ ), 1.6 times as strong

as 2-methoxybenzoic acid; and 3:5-dichloro-2-methoxybenzoic acid ( $166\cdot5^\circ$ ), 10 times as strong as 5-chloro-2-ethoxybenzoic acid.

2-Chloro-3-hydroxybenzoic acid ( $156\text{--}157^\circ$ ) and 6-chloro-3-hydroxybenzoic acid ( $178^\circ$ ) have equal affinity constants which are almost the same as that of 6-chloro-3-methoxybenzoic acid ( $168\text{--}169^\circ$ ); 2:6-dichloro-3-hydroxybenzoic acid ( $122\text{--}124^\circ$ ) has an affinity about 16 times as great as these. 2-Chloro-6-bromo-3-hydroxybenzoic acid ( $116\text{--}118^\circ$ ) has almost the same affinity as 2:6-dichloro-3-hydroxybenzoic acid, which confirms the constitution given by Martini (this vol., i, 150). Only about 1—1·5 per cent. of these acids are esterified by Fischer and Speier's method (Abstr., 1896, i, 201), whilst Martini's 6-chloro-2-bromo-3-hydroxybenzoic acid ( $194\text{--}195^\circ$ ) (*loc. cit.*) has an affinity 12 times as great as those of its two isomerides, and can be esterified to the extent of more than 70 per cent. by either V. Meyer's or Fischer and Speier's method; hence the bromine atom cannot be in the position 2, but must be at either 4 or 5.

3-Chloro-4-hydroxybenzoic acid ( $169\text{--}170^\circ$ ) has an affinity constant about double that of *p*-hydroxybenzoic acid; this is about the same change as is produced when a chlorine atom enters in the meta-position to the carboxyl in either benzoic or salicylic acid.

The two dichloroprotocatechuic acids, ( $+3\text{H}_2\text{O}$ ,  $220^\circ$ ) and ( $239^\circ$ ), show, when the dilution is great, almost equal affinities, and these are about the same as that of dichloroveratric acid ( $182\text{--}183^\circ$ ).

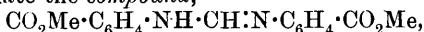
The methyl ( $+1\frac{1}{4}\text{H}_2\text{O}$ ,  $193^\circ$ ) and ethyl ( $+2\frac{1}{2}\text{H}_2\text{O}$ ,  $155^\circ$ ) esters of gallic acid have about equal dissociation constants, greater than that of pyrogallol. The affinity of the methyl ester of monochlorogallic acid ( $+ \text{H}_2\text{O}$ ,  $159\text{--}160^\circ$ ) is about 2·6 times, and that of the ethyl ester ( $+ \text{H}_2\text{O}$ ,  $106\text{--}107^\circ$ ) about twice, that of the corresponding gallic ester. The methyl ( $+1\frac{1}{2}\text{H}_2\text{O}$ ,  $160\text{--}170^\circ$ ) and ethyl ( $+1\frac{1}{2}\text{H}_2\text{O}$ ,  $151\text{--}153^\circ$ ) dichlorogallates have respectively 2·4 and 2·33 times the affinities of the above corresponding monochloro-compounds; methyl dibromogallate ( $+1\frac{1}{2}\text{H}_2\text{O}$ ,  $169^\circ$ ) gives still higher values for the affinity constant. The results obtained with ethyl dibromogallate ( $+1\frac{1}{2}\text{H}_2\text{O}$ ,  $137^\circ$ ) and methyl ( $+1\frac{1}{2}\text{H}_2\text{O}$ ,  $162\text{--}163^\circ$ ) and ethyl ( $+1\frac{1}{2}\text{H}_2\text{O}$ ,  $134\text{--}135^\circ$ ) chlorobromogallates were unsatisfactory.

T. H. P.

**Reactions of Hydrocoumarone.** By JOHANNES BOES (*Chem. Centr.*, 1902, ii, 370; from *Apoth.-Zeit.*, 17, 422).—Hydrocoumarone dissolves in concentrated sulphuric acid, forming a yellowish-red solution. The sulphonic acid and its salts are difficult to obtain in a crystalline form. *Hydrocoumaronesulphonic chloride* crystallises from alcohol in needles and melts at  $81^\circ$ . *Hydrocoumaronesulphonamide*,  $\text{C}_8\text{H}_9\text{O}_3\text{NS}$ , crystallises from alcohol and melts at  $163^\circ$ . Attempts to isolate an isomeric sulphonamide failed. Hydrocoumarone resembles hydrindene in its behaviour towards halogens, forming monohalogen hydrocoumarones, which have penetrating odours and do not boil under the ordinary pressure without decomposition. When sodium hydrocoumaronesulphonate is fused with potassium hydroxide, a hydroxy-compound is formed.

E. W. W.

**Anæsthetics.** By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1902, **26**, 743).—From *p*-phenetidine and its homologues and ethyl orthoformate, compounds of the type of methenyldi-*p*-phenetidine have been prepared which have an anæsthetic action. From *p*-aminobenzoic acid and ethyl orthoformate, by 10 minutes' boiling in alcoholic solution, a compound,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , is obtained; it melts at  $235^\circ$ , and is soluble in alkalis and alkali carbonates; it acts both as an anæsthetic and an antiseptic. The analogous compound from *m*-aminobenzoic acid melts at  $250^\circ$ . From ethyl *p*-aminobenzoate and ethyl orthoformate the compound,



melting at  $240^\circ$ , and the compound,  $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}(\text{OEt})_2$ , melting at  $209^\circ$ , are obtained. Methyl *p*-aminobenzoate reacts with formaldehyde in the presence of hydrogen chloride, yielding the compound,  $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\text{Cl}$ , which, with alkalis, gives an amorphous base.

K. J. P. O.

**Direct Conversion of Cinnamic Acid into  $\alpha$ -Truxillic Acid.** By C. N. RIIBER (*Ber.*, 1902, **35**, 2908—2909).—Liebermann (*Abstr.*, 1895, i, 470) showed that cinnamylidenemalononic acid was converted under the influence of light into an isomeric acid, which the author (this vol., i, 617) has proved to be a tetramethylene derivative; on oxidation, the latter yields  $\alpha$ -truxillic acid. Since both cinnamic and  $\alpha$ -truxillic acids are found in the leaves of *Erythroxylon coca*, it seemed possible that the action of light on the former gave rise to the formation of the latter acid. Very finely powdered cinnamic acid was exposed to light for three-and-a-half weeks, during which, however, there were only 50 hours of bright sunshine. Seventy per cent. of the acid was found to have been changed into  $\alpha$ -truxillic acid,  $\text{C}_{18}\text{H}_{16}\text{O}_4$ , which crystallised in needles melting at  $275^\circ$ , and yielded a methyl ester (m. p.  $173^\circ$ ). On distillation, cinnamic acid is re-formed.

K. J. P. O.

**Dibromo- $\alpha$ -truxillic Acid.** By R. KRAUSS (*Ber.*, 1902, **35**, 2931—2933).—*Ethyl dibromotruxillate*,  $\text{C}_{22}\text{H}_{22}\text{O}_4\text{Br}_2$ , crystallises from alcohol in colourless needles and melts at  $124$ — $126^\circ$ . The acid,  $\text{C}_{18}\text{H}_{14}\text{O}_4\text{Br}_2$ , crystallises from acetic acid in small, colourless needles, melts at  $260$ — $264^\circ$ , does not reduce permanganate, but when distilled is converted into bromocinnamic acid, which can then be oxidised to *p*-bromobenzoic acid. The constitution

$$(p)\text{C}_6\text{H}_4\text{Br}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$$

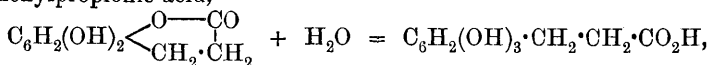
$$\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Br}(p)$$

is therefore assigned to the acid.

T. M. L.

**Dyes of the *Æsculetin* Series. II.** By CARL LIEBERMANN and S. LINDENBAUM (*Ber.*, 1902, **35**, 2919—2923. Compare *Abstr.*, 1901, i, 736).—When reduced in small quantities with sodium amalgam at  $100^\circ$  in a stream of carbon dioxide, *æsculetin* gives hydro $\alpha$ *æsculetin* and *æsculetin dihydride*,  $\text{C}_9\text{H}_8\text{O}_4$ ; the latter, which was separated by extracting the acidified solution with ether, crystallises from hot water in white flakes and melts at  $198$ — $200^\circ$ ; it is only slightly soluble in cold, but dissolves easily in hot, water, and partially remains in

solution; similarly, when dissolved in ether, it separates as an oil and only becomes crystalline when heated; it is therefore probable that it adds on a mol. of water, perhaps with formation of a trihydroxy-phenylpropionic acid,



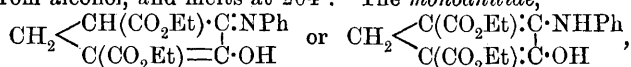
and is dehydrated on heating. The dihydride is not identical with Schiff's para-æsculetin (*Annalen*, 1872, 161, 84), and when treated with ammonia exhibits a striking series of colour reactions.

T. M. L.

**1:2-Diketopentamethylene** ( $\Delta^2$ -cyclopentene-1-one-2-ol) and **Derivatives**. By WILHELM DIECKMANN (*Ber.*, 1902, 35, 3201—3217). —Ethyl 1:2-diketopentamethylene-3:5-dicarboxylate (Abstr., 1894,

i, 324),  $\text{CH}_2 \begin{array}{c} \text{C}(\text{CO}_2\text{Et}) \cdot \text{C} \cdot \text{OH} \\ \diagdown \quad \diagup \\ \text{C}(\text{CO}_2\text{Et}) \cdot \text{C} \cdot \text{OH} \end{array}$ , has strongly acid properties; its aqueous alcoholic solution reddens blue litmus, it dissolves in dilute alkalis and alkali carbonates and also dissolves readily in sodium acetate solution; dry ammonia precipitates the ammonium salt as a colourless powder; it is stable towards alkalis and is not hydrolysed by concentrated hydrochloric acid; the sodium derivative,  $\text{CH}_2 \begin{array}{c} \text{C}(\text{CO}_2\text{Et}) \cdot \text{C} \cdot \text{ONa} \\ \diagdown \quad \diagup \\ \text{C}(\text{CO}_2\text{Et}) \cdot \text{C} \cdot \text{ONa} \end{array}$ , is

only slightly soluble in excess of alkali and is obtained either anhydrous or with  $1\frac{1}{2}\text{H}_2\text{O}$ ; the iron salt forms a dark brownish-red, crystalline powder which dissolves sparingly with a violet coloration in ether. The copper derivative,  $\text{C}_{11}\text{H}_{13}\text{O}_6\text{Cu}$ , is a clear green, crystalline salt insoluble in all solvents and melts at  $230^\circ$ . The osazone,  $\text{C}_{23}\text{H}_{16}\text{O}_4\text{N}_4$ , crystallises from alcohol in minute, yellow needles and melts at  $112^\circ$ . The phenazine,  $\text{C}_{17}\text{H}_{18}\text{O}_4\text{N}_2$ , separates on warming an alcoholic solution of the ester with *o*-phenylenediamine in minute, yellow needles, crystallises from alcohol, and melts at  $204^\circ$ . The monoanilide,



separates from methyl alcohol in yellowish crystals, melts at  $107^\circ$ , dissolves in alkalis, and is precipitated unchanged by acids.

**1:2-Diketopentamethylene**,  $\text{CH}_2 \begin{array}{c} \text{CH} \cdot \text{C} \cdot \text{OH} \\ \diagdown \quad \diagup \\ \text{CH}_2 \cdot \text{CO} \end{array}$  (Abstr., 1897, i, 462), is best prepared by hydrolysing the ester with 20 per cent. sulphuric acid; it is oxidised by alkaline hydrogen peroxide to glutaric acid. The benzoyl derivative,  $\text{CH}_2 \begin{array}{c} \text{CH} \cdot \text{C} \cdot \text{OBz} \\ \diagdown \quad \diagup \\ \text{CH}_2 \cdot \text{CO} \end{array}$ , separates from methyl alcohol in colourless crystals and melts at  $72\text{--}73^\circ$ . The phenylurethane,  $\text{CH}_2 \begin{array}{c} \text{CH} \cdot \text{C} \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh} \\ \diagdown \quad \diagup \\ \text{CH}_2 \cdot \text{CO} \end{array}$ , crystallises from benzene and melts at

$122^\circ$ . The phenazine derivative,  $\text{CH}_2 \begin{array}{c} \text{CH}_2 \cdot \text{C} \cdot \text{N} \\ \diagdown \quad \diagup \\ \text{CH}_2 \cdot \text{C} \cdot \text{N} \end{array} \text{C}_6\text{H}_4$ , separates from alcohol or water in colourless needles, melts at  $102\text{--}103^\circ$ , and distils without decomposition at about  $290^\circ$ ; its solubility in water reaches a maximum at  $70^\circ$ .

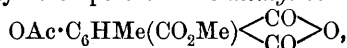
*Phenylazo-1 : 2-diketopentamethylene*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CO} \text{---} \text{CO} \end{array} > \text{C} : \text{N} \cdot \text{NHPH}$  or  $\begin{array}{c} \text{CH}_2 \text{---} \text{CH}_2 \\ | \quad | \\ \text{CO} : \text{C}(\text{OH}) \end{array} > \text{C} : \text{N} : \text{NPh}$ , forms a red, crystalline precipitate, melts at  $130^\circ$ , and dissolves readily in alkalis and alkali carbonates.

*3-Chloro-1 : 2-diketopentamethylene*,  $\text{CH}_2 < \begin{array}{c} \text{CCl} : \text{C} \cdot \text{OH} \\ | \quad | \\ \text{CH}_2 \cdot \text{CO} \end{array}$ , is probably identical with the compound which Hantzsch (Abstr., 1889, 853) described as chloro-1 : 3-diketopentamethylene. *Chlorodibromo-1 : 2-diketopentamethylene*, probably  $\text{CH}_2 < \begin{array}{c} \text{CCl} = \text{C} \cdot \text{OH} \\ | \quad | \\ \text{CBr}_2 \cdot \text{CO} \end{array}$ , prepared by brominating the preceding compound, crystallises from carbon tetrachloride or water and melts at  $121\text{--}122^\circ$ . *3-Anilino-1 : 2-diketopentamethylene-2-monoanil hydrochloride*,  $\text{CH}_2 < \begin{array}{c} \text{CH}_2 \cdot \text{C} \cdot \text{NHPH} \\ | \quad | \\ \text{CO} \text{---} \text{C} \cdot \text{NHPH}, \text{HCl} \end{array}$ , prepared by the action of aniline on a solution of the chloro-compound in acetic acid, forms yellow, crystal flakes, and becomes brown and decomposes and melts at  $260^\circ$ .

*3-Bromo-1 : 2-diketopentamethylene* melts at  $155^\circ$ . *3 : 5 : 5-Tribromo-1 : 2-diketopentamethylene* forms colourless crystals and melts at  $155^\circ$ .

T. M. L.

**Acetylation of Cochenillic Acid.** By CARL LIEBERMANN and S. LINDENBAUM (*Ber.*, 1902, 35, 2910—2919).—An *acetylcochenillic anhydride*,  $\text{OAc} \cdot \text{C}_6\text{HMe}(\text{CO}_2\text{H}) < \begin{array}{c} \text{CO} \\ | \quad | \\ \text{CO} \end{array} > \text{O}$  [4 : 6 : 1 : 2 : 3 or 4 : 6 : 3 : 1 : 2], is obtained by acetylating cochenillic acid with a mixture of acetic anhydride and acetyl chloride; it crystallises from acetic acid in colourless plates and melts and decomposes at  $152\text{--}153^\circ$ . The *silver salt*,  $\text{C}_{12}\text{H}_7\text{O}_7\text{Ag}$ , forms minute, white needles, is somewhat soluble in water, and is readily decomposed. The *methyl ether*,



from the silver salt and methyl iodide, crystallises from ether in plates and melts at  $136\text{--}138^\circ$ .

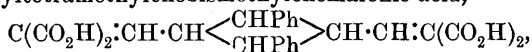
*Dimethyl acetylcochenillate*,  $\text{OAc} \cdot \text{C}_6\text{H}(\text{CO}_2\text{Me})_2 \cdot \text{CO}_2\text{H}$ , prepared by boiling the preceding substance with methyl alcohol, crystallises from ether and melts at  $149^\circ$ .

By acetylating with acetyl chloride, only an *acetylcochenillic acetic anhydride*,  $\text{OAc} \cdot \text{C}_6\text{HMe}(\text{CO}_2\text{H})_2 \cdot \text{CO} \cdot \text{OAc}$ , was obtained in large, clear crystals which gradually became opaque; it softens and melts with decomposition at  $230^\circ$ . When exposed to air, it is hydrolysed into acetic acid and *acetylcochenillic acid*; the latter melts at  $118\text{--}124^\circ$ , resolidifies, and melts again with decomposition at  $220^\circ$ .

*Trimethyl acetylcochenillate*,  $\text{OAc} \cdot \text{C}_6\text{HMe}(\text{CO}_2\text{Me})_3$ , prepared by heating the preceding compound with silver oxide and methyl iodide, crystallises from dilute acetic acid in needles and melts at  $106\text{--}108^\circ$ . It is hydrolysed by decinormal sodium hydroxide, giving *trimethyl cochenillate*,  $\text{OH} \cdot \text{C}_6\text{HMe}(\text{CO}_2\text{Me})_3$ , which forms white needles, crystallises from water, melts at  $136\text{--}138^\circ$ , and gives a violet coloration with ferric

chloride. By heating acetylcochenillic acid or its acetic anhydride at 70—80°, an *acetylcochenillic anhydride* is obtained isomeric with that described above; it melts at 140—148°, and on exposure to air is hydrolysed to acetylcochenillic acid; the latter, when heated at 115°, is converted, by the loss of a mol. of water, into *cochenillic anhydride*,  $\text{OH}\cdot\text{C}_6\text{HMe}(\text{CO}_2\text{H})\langle\begin{smallmatrix}\text{CO}\\\text{CO}\end{smallmatrix}\rangle\text{O}$ , melting at 215—223° with decomposition. *Benzoylcochenillic anhydride*,  $\text{OBz}\cdot\text{C}_6\text{HMe}(\text{CO}_2\text{H})\langle\begin{smallmatrix}\text{CO}\\\text{CO}\end{smallmatrix}\rangle\text{O}$ , crystallises from benzene and melts at 187—189°. T. M. L.

**Action of Light on Cinnamylidenemalonic Acid.** By ELMER P. KOHLER (*Amer. Chem. J.*, 1902, 28, 233—240).—An investigation of the white compound obtained by Liebermann (*Abstr.*, 1895, i, 470) by the action of light on cinnamylidenemalonic acid has shown that it is a diphenyltetramethylenebismethylenemalonic acid,



a conclusion already arrived at by Riiber (this vol., i, 617). This acid readily combines with 2 mols. of hydrogen chloride; when its solution in methyl alcohol is saturated with hydrogen chloride, a *methyl ester*,  $\text{C}_{28}\text{H}_{30}\text{O}_8\text{Cl}_2$ , is produced which is soluble in hot acetone, crystallises in thick needles, and melts and decomposes at 197—198°; the corresponding *ethyl ester*,  $\text{C}_{30}\text{H}_{34}\text{O}_8\text{Cl}_2$ , melts and decomposes at 185°. When the acid is treated with bromine, an unstable additive compound is produced, which decomposes with elimination of carbon dioxide and hydrogen bromide and formation of *diphenyltetramethylenebisbromomethyleneacetic acid*,  $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CBr}\cdot\text{CH}\langle\begin{smallmatrix}\text{CHPh}\\\text{CHPh}\end{smallmatrix}\rangle\text{CH}\cdot\text{CBr}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ ;

the last-mentioned substance crystallises in colourless plates, melts and decomposes at 245°, is readily soluble in alcohol or acetone, and yields  $\alpha$ -truxillic acid on oxidation with alkaline permanganate; its *methyl ester* melts at 115°. Diphenyltetramethylenebismethylenemalonic acid unites with 2 mols. of potassium hydrogen sulphite with formation of an additive compound. When the acid is dissolved in concentrated sulphuric acid and the solution is poured into water, cinnamylidenemalonic acid is precipitated. E. G.

**Study of Lichens. X.** By WILHELM ZOPF (*Annalen*, 1902, 324, 39—78. Compare *Abstr.*, 1899, i, 716).—The name *protolichesteric acid* is given to a colourless, acidic substance obtained from *Cetraria cucullata*, this lichen yielding 2.2 per cent. of the compound, whilst *C. chlorophylla* furnishes only 0.5 per cent.; this acid can also be extracted from *C. complicata* and *C. islandica*, provided that ether is employed and not alcohol: the latter solvent causes the transformation of the substance into its isomeride, lichesteric acid (m. p. 124—125°); this change is also effected by hot acetic anhydride. Protolichesteric acid,  $\text{C}_{18}\text{H}_{32}\text{O}_5$ , crystallises from benzene, light petroleum, ether, or alcohol in nacreous, rhombic leaflets melting at 103—104°. When separating slowly from dilute alcoholic solutions, it assumes the form of pyramidal, hemimorphous, rhombic crystals having an extinction parallel

to the principal axis. The acid has  $\alpha_D$  12.1° at 19.5°, it dissolves in sodium hydrogen carbonate solution and in the presence of alkalis immediately decolorises potassium permanganate. Mineral acids reprecipitate the unchanged substance from its solutions in the alkali hydroxides, and although partly transformed into amorphous products, protolichestic acid is not converted into lichestic acid when heated above its melting point.

In *C. chlorophylla*, protolichestic acid is accompanied by a small quantity of atranoric acid. *C. complicata* also furnished protocetraric, *l*-usnic, and atranoric acids. The lichestic acid, isolated from *C. islandica* by Schnedermann and Knop, is in reality the product of the transformation of protolichestic acid, and when ether or benzene is employed in the extraction only the latter substance is obtained.

The amorphous dilichestic acid extracted from *C. islandica* var. *vulgaris* by Hesse is a decomposition product of protolichestic acid formed by treating the latter substance with glacial acetic acid at 80°.

*C. tubulosa* (*C. juniperina* var. *tubulosa*) yields usnic, vulpic, and pinastric acids, the last being identical with the substance isolated from *C. pinastris*. In addition to these compounds, *C. tubulosa* furnishes a new substance, *cetrarialic acid* which separates in lustrous, pale olive-brown leaflets sparingly soluble in cold alcohol, ether, or benzene, but dissolving more readily on warming. In dilute potassium hydroxide solution, the new acid dissolves with evolution of gas; it is also soluble in an aqueous solution of sodium hydrogen carbonate.

Barbatic acid, isolated from *Usnea longissima* (Abstr., 1898, i, 99), forms a characteristic sodium salt which crystallises in rosettes of flattened, curvilinear needles. *U. cornuta* yields *d*-usnic and usnaric acids, the latter in larger quantity. *U. ceratina*, obtained from the pine trees of the Black Forest at an altitude of 700–800 metres, furnishes only barbatic acid and a trace of usnic acid; this result is contrary to that of Hesse (Abstr., 1895, i, 298), the latter observer stating that barbatin and a large quantity of usnic acid are obtainable from the lichen. *U. dasypoga* accompanies the preceding species and yields barbatic, *d*-usnic, and usnaric acids, but not alecortic acid (compare Hesse, Abstr., 1900, i, 149). *Parmelia sinuosa* contains *d*-usnic acid and probably usnaric acid.

Thamnolic acid, a substance isolated from *Thamnolia vermicularis* when heated at 50–60° with concentrated hydrochloric acid, yields *thamnolin*, a reddish-brown, microcrystalline substance dissolving in hot water, alcohol, chloroform, or glacial acetic acid to a red solution. This product is also sparingly soluble in ether or benzene and develops a reddish-brown coloration with ammoniacal or alkaline solutions; it is reprecipitated by hydrochloric acid, but not by carbon dioxide.

*Cladina uncialis* contains *d*-usnic and thamnolic acids, the former being identified by conversion into usnolic acid and the latter by the thamnolin reaction.

Squamatic acid, hitherto only obtained by Hesse from *Cladonia squamosa*, has also been isolated from *C. glauca*.

The presence of patellaric acid in *Urceolaria scruposa* has been confirmed; it crystallises from 50 per cent. alcohol in flattened plates and decomposes at 165°. This acid gives a bluish-red coloration with

bleaching powder and also develops an intense blue coloration with a solution of barium hydroxide or hydrated barium peroxide. Lecanoric acid has the same melting point and develops a similar coloration with bleaching powder, but not with barium hydroxide or peroxide. Olivetoric acid develops a bluish-green coloration with the latter of these reagents, but not with the former. Patellaric acid dissolves in sodium hydrogen carbonate and cold barium hydroxide solutions without decomposition and acids regenerate the unaltered substance; when heated with dilute potassium hydroxide solution, it develops a yellow coloration which then becomes red, and on adding a few drops of chloroform the liquid acquires a deep green fluorescence, which is rendered more distinct by cooling and diluting.

Lecanoric and atranoric acids could not be detected in the extracts from *U. scruposa*.  
G. T. M.

**Reduction of Carboxylic Derivatives to Aldehydes and their Derivatives and to Amines.** By FRANZ HENLE (*Ber.*, 1902, 35, 3039—3044).—The hydrochlorides of the imino-ethers are readily reduced by sodium amalgam and dilute acids to the corresponding aldehydes. If the reduction be carried on in presence of phenylhydrazine or semicarbazide, the corresponding hydrazone or semicarbazone is obtained. Benzimino-ethyl ether hydrochloride is readily converted in this way into benzaldehyde, the yield amounting to 23·5 per cent. of the theoretical. In the presence of phenylhydrazine, the yield of benzylidenehydrazone is quantitative, and this reaction can readily be demonstrated, a voluminous precipitate of the hydrazone being formed. In the presence of semicarbazide, a yield of 52 per cent. of the theoretical amount of semicarbazone is obtained. In a similar manner, acetimino-ethyl ether hydrochloride yields 40 per cent. of the theoretical amount of ethylidenephénylhydrazone. In the absence of phenylhydrazine, the chief reaction is the hydrolysis of the imino-ether, but a certain amount of acetaldehyde is also produced.

Since phenylhydrazones can be reduced to amines, this reaction affords a new method of passing from the nitriles to the primary amines, all the operations being carried out at low temperatures.

Benzamidine hydrochloride is reduced by sodium amalgam and hydrochloric acid to benzylamine, the yield amounting to 38 per cent. of the theoretical.  
A. H.

***op*-Dinitrobenzaldehyde.** By PAUL FRIEDLÄNDER and PAUL COHN (*Monatsh.*, 1902, 23, 543—562).—*op*-Dinitrobenzyl chloride is obtained in an almost quantitative yield when *p*-nitrobenzyl chloride is nitrated with a slight excess of nitric acid in concentrated sulphuric acid (compare Krassusky, *J. Russ. Phys. Chem. Soc.*, 1895, 27, 335). It forms rhombic crystals, melts at 34°, is insoluble in water, sparingly soluble in light petroleum, but easily so in other ordinary solvents. It has little odour and is only slightly volatile with steam. *op*-Dinitrobenzylaniline, formed from *op*-dinitrobenzyl chloride and aniline in alcoholic solution, crystallises from benzene in orange-red crystals, melts at 132°, and forms a *hydrochloride* which crystallises in



colourless needles or leaflets and is dissociated by water, and a *platinichloride* which is easily soluble in water. *op-Dinitrobenzyl-p-toluidine* crystallises from alcohol in delicate, red needles and melts at 93°. *op-Dinitrobenzyl- $\alpha$ -naphthylamine* crystallises from glacial acetic acid in dark red scales and melts at 164°. *op-Dinitrobenzylaniline-p-sulphonic acid* crystallises in yellow needles, is moderately soluble in water, and less readily so in alcohol; the *barium* and *silver* salts are described.

*op-Dinitrobenzyl acetate* crystallises in glistening, four-sided, thick plates, melts at 96—97°, is easily soluble in alcohol, benzene, or glacial acetic acid, but insoluble in light petroleum, and is hydrolysed by dilute sulphuric acid to *op-dinitrobenzyl alcohol*, which crystallises from alcohol in glistening, lemon-yellow needles, melts at 114—115°, and is easily soluble in alcohol, benzene, or glacial acetic acid, but insoluble in light petroleum. The action of nitric acid on *p*-nitrobenzyl alcohol dissolved in sulphuric acid leads to the formation of *p*-nitrobenzyl nitrate, and not of dinitrobenzyl alcohol. *p-Nitrobenzyl hydrogen sulphate* is formed when the alcohol is dissolved in concentrated sulphuric acid.

*op-Dinitrobenzaldehyde*, formed by oxidation of dinitrobenzylaniline-sulphonic acid with sodium dichromate in sulphuric acid solution, crystallises from a mixture of benzene and light petroleum in glistening plates, which become matt on exposure to light, melts at 68—69°, is easily soluble in most solvents, but sparingly so in water or light petroleum, and is only slightly volatile with steam. When warmed with sodium carbonate solution, the aldehyde is decomposed, with formation of a brown substance; with sodium hydrogen sulphite, it forms a crystalline compound easily soluble in water, and with phenylhydrazine in alcoholic solution it forms a *phenylhydrazone*, which crystallises in reddish-brown, hair-like needles, melts at 227—228°, and is sparingly soluble in the usual solvents. *op-Dinitrobenzylideneaniline*, formed from dinitrobenzaldehyde and aniline, crystallises from glacial acetic acid in thick, glistening, orange-yellow needles, melts at 131—132°, and is easily soluble in benzene or acetic acid, more sparingly so in alcohol. *op-Dinitrobenzylidene-p-toluidine* crystallises from glacial acetic acid in yellow needles and melts at 151°. *op-Dinitrobenzylidene- $\alpha$ -naphthylamine* crystallises in orange-red needles, melts at 202°, and is sparingly soluble in alcohol or glacial acetic acid. *op-Dinitrobenzaldoxime* crystallises from hot water in glistening, silky needles, melts at 127—128°, and is easily soluble in benzene, with a slight green colour, in the usual solvents, and in sodium hydroxide solution. The *benzoyl* derivative crystallises from glacial acetic acid in small, slightly yellow needles, sinters and melts at 165—166°. On prolonged boiling with acetic anhydride, the aldoxime is converted into *dinitrobenzonitrile*, which crystallises from alcohol in glistening, slightly brownish-yellow, rhombic plates, melts at 104—105°, and is easily soluble in ether, alcohol or benzene, but less readily so in carbon disulphide. *op-Dinitrobenzamide*, formed from the nitrile by the action of warm concentrated sulphuric acid, crystallises from water in long, glistening, slightly green needles, melts at 203—204°, and is converted by nitrous acid in 50 per cent. sulphuric acid solution into dinitrobenzoic acid, which is also formed

when dinitrobenzaldehyde is boiled with silver acetate in acetic acid solution.

*o*-Nitroso-*p*-nitrobenzoic acid is formed from dinitrobenzaldehyde when its solution in benzene is exposed to direct sunlight. The nitroso-compound crystallises from ethyl acetate in glistening, slightly greenish-yellow leaflets, melts above  $300^{\circ}$ , and is sparingly soluble in the usual solvents, forming grass-green solutions when warmed. With aniline, it forms a yellowish-red azo-compound, and with methyl sulphate a methyl ester which crystallises from dilute acetic acid in glistening, yellow, silky needles, melts at  $137$ — $138^{\circ}$ , and is more soluble than the acid. G. Y.

**Condensation of Methyl Propyl Ketone with Benzaldehyde.** By CARL D. HARRIES and P. BROMBERGER (*Ber.*, 1902, 35, 3088—3090).—When these substances react in presence of dilute sodium hydroxide solution, *benzylidenemethyl propyl ketone*,  $\text{CHPh}\cdot\text{CH}\cdot\text{COPr}$ , is formed as a yellowish oil which boils at  $275^{\circ}$  and has a sp. gr. 0.9979 at  $17^{\circ}$ ; its *phenylhydrazone* melts at  $99$ — $100^{\circ}$ , its *semicarbazone* at  $150^{\circ}$ , and its *oxime* at  $97^{\circ}$ . The oxime gives a *dibromo*-compound (m. p.  $158^{\circ}$ ) when treated with bromine. On reduction, it yields the corresponding saturated ketone as a colourless oil which boils at  $130^{\circ}$  under 18 mm. pressure and has a sp. gr. 0.9614 at  $17^{\circ}$ .

In presence of hydrochloric acid, the condensation takes place to *benzylidenepropyl methyl ketone*,  $\text{CH}_2\text{Me}\cdot\text{C}(\text{CHPh})\cdot\text{COMe}$ , a yellow oil which distils at  $120$ — $130^{\circ}$  under 18 mm. pressure and has a sp. gr. 1.0216 at  $17^{\circ}$ . Its *oxime* melts at  $85^{\circ}$ , its *phenylhydrazone* at  $86^{\circ}$ , and its *semicarbazone* at  $207^{\circ}$ . J. McC.

[Derivatives of] **Hydroxybenzophenone.** By FRITZ ULLMANN and IRMA GOLDBERG (*Ber.*, 1902, 35, 2811—2814. Compare Graebe and Ullmann, *Abstr.*, 1896, i, 440).—*o*-Hydroxyphenyl *p*-tolyl ketone,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}$ , produced by condensing *o*-methoxybenzoyl chloride with toluene in the presence of aluminium chloride, separates from alcohol in large crystals, melting at  $61.5^{\circ}$ , and dissolving in sodium hydroxide solution to form a yellow sodium derivative; the *benzoyl* derivative melts at  $80^{\circ}$ ; the *phenylhydrazone* and the *dibromo*-compound form yellow crystals melting at  $145^{\circ}$  and  $132.5^{\circ}$  respectively; the *oxime* is a white substance melting at  $175^{\circ}$ .

3-Methoxybenzophenone,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$ , prepared from *m*-methoxybenzoyl chloride and benzene, boils at  $342$ — $343^{\circ}$  under 730 mm. pressure, and solidifies to a crystalline mass melting at  $37^{\circ}$ ; it is hydrolysed to 3-hydroxybenzophenone by hydrobromic acid.

4-Methoxybenzophenone,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$ , obtained by employing *p*-methoxybenzoyl chloride in the preceding condensations, boils at  $354$ — $355^{\circ}$  under 729 mm. pressure (compare Gattermann, *Abstr.*, 1890, 962). G. T. M.

**Synthesis of Two Benzoylxylenols.** By PIETRO BARTOLOTTI and ADOLFO LINARI (*Gazzetta*, 1902, 32, i, 494—503).—6-Benzoyl-1:4:2-xenol,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{C}\begin{smallmatrix} \text{CMe}\cdot\text{C}(\text{OH}) \\ \text{CH}=\text{CMe} \end{smallmatrix}\text{CH}$ , was prepared by first

benzoylating 1:4:2-xylenol by Baumann's method, then heating the benzoyl compound with benzoyl chloride and zinc chloride, by which means benzoylxylenyl benzoate was obtained; the latter compound was then hydrolysed with aqueous alcoholic sodium hydroxide. Benzoyl-1:4:2-xylenol is deposited from alcohol in yellowish, shining scales melting at 166—167°; it is soluble in alkali hydroxides, giving a yellow coloration, but in dilute alcoholic solution it gives no coloration with ferric chloride. Its *acetyl* derivative,  $C_{17}H_{16}O_3$ , separates from aqueous alcohol in large, tabular, colourless crystals melting at 62—62.5°. The *methyl ether* is a dense, colourless liquid which boils at 194—195° under about 10 mm. pressure and is soluble in the ordinary solvents.

*Benzoyl-1:2:4-xylenol*,  $C_6H_5 \cdot CO \cdot C \begin{smallmatrix} \text{CMe} - \text{CMe} \\ \text{CH} : C(OH) \end{smallmatrix} CH$ , prepared in a similar manner to its isomeride, separates from alcohol in yellow crystals which melt at 110—111° and are soluble in the ordinary solvents; it colours the alkali hydroxides yellow, and in aqueous alcoholic solution gives an intense black coloration with ferric chloride. Its *benzoyl* derivative,  $C_{22}H_{18}O_3$ , is deposited from alcohol in colourless crystals which melt at 110° and are soluble in the ordinary solvents. The *acetyl* compound,  $C_{17}H_{16}O_3$ , crystallises from dilute alcohol in shining, colourless scales melting at 74—74.5°. The *methyl ether*,  $C_{16}H_{16}O_2$ , separates from alcohol in colourless crystals melting at 82.5—83°.

T. H. P.

**Hydroxy-derivatives of  $\alpha$ -Naphthaquinone.** By PAUL FRIEDLÄNDER and L. SILBERSTERN (*Monatsh.*, 1902, 23, 513—533).—1:8-Aminonaphthol, formed by melting 1:8-aminonaphthalene-sulphonic acid with sodium hydroxide (D.R.-P. 55404), crystallises from light petroleum in white needles, becomes grey on exposure to air, and melts and blackens at 94—97°. The *sulphate*,  $(C_{10}H_9ON)_2 \cdot H_2SO_4$ , separates from hot water in very slightly soluble crystals; the *hydrochloride* is sparingly soluble in concentrated hydrochloric acid and forms colourless crystals, which become grey on exposure to air. The *acetyl* derivative,  $OH \cdot C_{10}H_6 \cdot NHAc$ , is soluble in aqueous alkalis, forms colourless crystals, and melts at 138°. With diazotised sulphanilic acid in acetic acid solution, aminonaphthol forms a red precipitate which, on reduction with zinc dust and dilute hydrochloric acid and treatment with ferric chloride, yields jugloe (8-hydroxy- $\alpha$ -naphthaquinone).

Naphthazarin (Will, Abstr., 1895, i, 668) is formed from 1:8-diaminonaphthalene, 1:8-dihydroxynaphthalene, or 1:8-aminonaphthol by condensation with 2 mols. of diazotised sulphanilic acid and reduction and oxidation of the product. With sodium hydroxide and 1 mol. of methyl sulphate, 2:3-dihydroxynaphthalene yields a mixture of the *mono*- and *di-methyl* ethers. The dimethyl ether is formed quantitatively by the action of 2 mols. of methyl sulphate. The monomethyl ether forms colourless needles, melts at 108°, has an odour resembling that of guaiacol, is easily soluble in the usual solvents, gives a green coloration with ferric chloride in alcoholic solution, and is volatile with steam. The dimethyl ether crystallises in colourless needles, melts at 115—116°, has an intense odour, and is slightly volatile with

steam. The *monoethyl* ether melts at 109—110°, the *diethyl* ether at 96—97°.

*Benzeneazodihydroxynaphthalene*, formed from 2:3-dihydroxynaphthalene and 1 mol. of benzenediazonium chloride, crystallises from alcohol in glistening needles, and dissolves in alkalis to a yellowish-brown solution which becomes bright yellowish-red on addition of acid.

1-*Amino-2:3-dihydroxynaphthalene*, formed by addition of 1 mol. of diazotised sulphanilic acid to 2:3-dihydroxynaphthalene and reduction of the product with stannous chloride and hydrochloric acid, separates from hot water in small, white crystals, decomposes at about 230°, and is soluble in aqueous alkalis and in acids. Oxidation of the amino-dihydroxynaphthalene by ferric chloride leads to the formation of a *quinone*,  $C_{20}H_{10}O_7$  (?), which decomposes at about 250°, does not sublime, dissolves in alkalis with an intense bluish-violet colour, is reprecipitated unchanged by acids, and yields a tarry reduction product from which the quinone is re-formed by action of ferric chloride.

The action of 2 mols. of diazotised sulphanilic acid on 2:3-dihydroxynaphthalene leads to the formation of a dye which gives greyish-violet solutions in acids, reddish-violet in alkalis, and is reduced by stannous chloride and hydrochloric acid to 1:4-*diamino-2:3-dihydroxynaphthalene*, which is unstable when free, but forms a sulphate crystallising in glistening leaflets and yielding an intensely blue precipitate when warmed in aqueous solution in contact with air. Oxidation of the diamino-base with ferric chloride leads to the formation of *isonaphthazarin*.

Fusion of  $\beta$ -naphthol-3:6:8-trisulphonic acid (Abstr., 1883, 737) with sodium hydroxide leads to the formation of two dihydroxynaphthalenedisulphonic acids. The one which forms a sparingly soluble sodium salt crystallising in delicate needles, gives a rapidly fading blue coloration with ferric chloride, and reduces silver nitrate, must be 2:8-dihydroxynaphthalene-3:6-disulphonic acid, as in dilute solution it gives an intense bluish-violet coloration and forms a dark blue precipitate on addition of formaldehyde and concentrated hydrochloric acid. This reaction is found to be general for 2:8-dihydroxynaphthalenes. 2:3-Dihydroxynaphthalene-6:8-disulphonic acid forms a soluble sodium salt, and a sparingly soluble *barium* salt, but gives a stable violet coloration with ferric chloride, but yields no characteristic reaction with formaldehyde and concentrated hydrochloric acid.

Prolonged fusion of the trisulphonic acid with sodium hydroxide results in the formation of 2:3:8-trihydroxynaphthalene-6-sulphonic acid; this reduces silver nitrate, gives with ferric chloride a green coloration, and with formaldehyde and concentrated hydrochloric acid a deep violet coloration and precipitate.

2:3:8-Trihydroxynaphthalene (D.R.-P. 112098), formed by heating the sulphonic acid with sulphuric acid at 180°, crystallises from xylene in yellow needles, melts at 175°, is easily soluble in water, alcohol, or ether, sparingly so in benzene or light petroleum, gives a dark blue coloration with ferric chloride in aqueous solution, and on warming with formaldehyde and hydrochloric acid forms a greyish-green precipitate. The *triacetyl* derivative forms green crystals, melts at 143—144°, and is easily soluble in benzene, glacial acetic acid, or alcohol, more sparingly so

in water, ether, or light petroleum. The *trimethyl ether*, prepared by the action of methyl sulphate and sodium hydroxide, crystallises from light petroleum in small prisms, melts at 127—128°, is insoluble in alkalis, and has, on warming, an odour resembling thymol.

When coupled with diazotised sulphanilic acid in dilute acetic acid solution, trihydroxynaphthalene forms an orange-red *dye* which, in solution, is changed to reddish-violet by sodium carbonate or ammonia, to bluish-violet by sodium hydroxide. On reduction of the dye with stannous chloride and hydrochloric acid, a *base* is obtained which forms a sparingly soluble, colourless, crystalline *sulphate* rapidly oxidised on exposure to air. Oxidation of the base with ferric chloride leads to the formation of a *quinone*,  $C_{10}H_4(OH)_2O_2$ , which crystallises from dilute alcohol in small, brownish-red, crossed needles, decomposes without melting at a high temperature, sublimes to a slight extent, gives with sodium carbonate a violet coloration, with sodium hydroxide a green coloration which disappears on warming, and forms a *diacetyl* derivative which crystallises from dilute acetic acid in golden-yellow leaflets, darkens at 55°, and melts at 65—67°. G. Y.

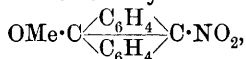
**Anthraquinone.** By K. DAMMANN and LUDWIG GATTERMANN (*Chem. Centr.*, 1902, ii, 368; from *Zeit. Farb. Textilchem.*, 1902, 1, 325—326).—The basic compounds formed by the action of dehydrating agents on  $\alpha$ -arylaminoanthraquinones have been regarded as acridine derivatives. This view is confirmed by the fact that the acridine derivative prepared from *o*-acridylbenzoic acid is identical with the compound obtained by the action of phosphoric acid on  $\alpha$ -anilinoanthraquinone. This *acridine* derivative,  $C_{20}H_{11}ON$ , prepared in the one case by boiling a solution of *o*-acridylbenzoic chloride in carbon disulphide with aluminium chloride, crystallises from a mixture of pyridine and methyl alcohol in orange-red leaflets and melts at 206°. E. W. W.

**Reactions of Aromatic Nitro-compounds.** By JAKOB MEISENHEIMER (*Annalen*, 1902, 323, 205—246).—*Anthraquinoneoximediethylacetal*,  $C(OMe)_2 \langle \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} \rangle C:NOH$ , is prepared by heating nitroanthracene with a solution of potassium hydroxide in methyl alcohol, diluting the product with water, and precipitating the oxime with carbon dioxide; it crystallises from benzene or methyl alcohol in pale yellow needles, melts at 171°, and dissolves in the ordinary organic solvents but not in water; the *acetyl* derivative decomposes at 114°; the *methyl ether* separates in colourless crystals melting at 96°, the *benzyl ether* crystallises in yellow needles and melts at 69—70°. *Anthraquinoneoximediethylacetal*, obtained by the action of an alcoholic potassium hydroxide solution on nitroethoxydihydroanthracene,  $OEt \cdot CH \langle \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} \rangle CH \cdot NO_2$ , separates from benzene in granular crystals and decomposes at 172—173°. *Anthraquinoneoximemethylethylacetal* is produced either by treating anthracene ethyl nitrate with potassium hydroxide dissolved in methyl alcohol or by the action of an alcoholic solution of the alkali hydroxide on nitromethoxydihydroanthracene; it forms colourless crystals and decomposes at 134—135°.

*Anthraquinonedimethylacetal*,  $\text{C(OMe)}_2\langle\text{C}_6\text{H}_4\rangle\text{CO}$ , results from the oxidation of anthraquinoneoximedimethylacetal with an alkaline solution of potassium ferricyanide; it crystallises in transparent prisms, melts at  $129^\circ$ , and is readily soluble in the ordinary organic solvents. When treated in methyl alcohol solution with a trace of dilute sulphuric acid, the preceding acetal yields anthraquinone.

Anthraquinoneoxime results when the product of the action of methyl alcohol and potassium hydroxide on nitroanthracene is acidified with a mineral acid instead of carbon dioxide.

Nitromethoxydihydroanthracene,  $\text{OMe}\cdot\text{CH}\langle\text{C}_6\text{H}_4\rangle\text{CH}\cdot\text{NO}_2$ , which is readily prepared by adding concentrated nitric acid to anthracene suspended in benzene and methyl alcohol, yields an unstable *potassium* derivative crystallising in colourless, lustrous needles; this substance dissolves in water or methyl alcohol, but on prolonged heating with these solvents it decomposes, yielding nitroanthracene; it may also be crystallised from benzene. This derivative is also obtained by shaking together powdered nitroanthracene and a methyl alcohol solution of potassium hydroxide. When treated with potassium hypobromite, the potassium derivative yields bromonitromethoxydihydroanthracene,  $\text{OMe}\cdot\text{CH}\langle\text{C}_6\text{H}_4\rangle\text{CBr}\cdot\text{NO}_2$ , a substance separating from ether in well-defined, colourless crystals decomposing at  $93^\circ$ ; this product, when boiled with methyl alcohol and potassium hydroxide, gives rise to nitromethoxyanthracene,



which crystallises in yellow needles and melts at  $156^\circ$ . This reaction also gives rise to a certain amount of nitroanthranol.

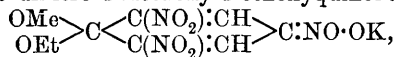
*Bromonitroanthronedimethylacetal*,  $\text{C(OMe)}_2\langle\text{C}_6\text{H}_4\rangle\text{CBr}\cdot\text{NO}_2$ , is produced by boiling nitromethoxyanthracene with a methyl alcohol solution of potassium hydroxide, diluting the liquid with water, and adding sodium hypobromite solution; it crystallises from methyl alcohol in white leaflets and decomposes at  $139\text{--}140^\circ$ . This acetal, unlike those previously described, is not affected by mineral acids.

*Oxanthranyl methyl ether*,  $\text{OMe}\cdot\text{CH}\langle\text{C}_6\text{H}_4\rangle\text{CO}$ , prepared by acidifying an ice-cold aqueous solution of the potassium derivative of nitromethoxydihydroanthracene with very dilute sulphuric acid, is separated from the nitroanthracene, also produced in this reaction, by successive crystallisation from chloroform and benzene; it crystallises from these solvents, or from the alcohols, in colourless prisms melting at  $102\cdot5^\circ$ , and is probably identical with the substance described by Liebermann as melting at  $98^\circ$  (compare Abstr., 1889, 715).

*isoNitromethoxydihydroanthracene*,  $\text{OMe}\cdot\text{CH}\langle\text{C}_6\text{H}_4\rangle\text{C}\cdot\text{NO}\cdot\text{OH}$ , is obtained from the preceding experiment when the first chloroform extract is evaporated at  $20\text{--}30^\circ$  under diminished pressure instead of

at 100°; on adding light petroleum to its chloroform solution, it separates in colourless, rhombic plates decomposing at 125°.

Potassium 3 : 5-dinitro-4-methoxy-4-ethoxyquinol-1-nitrolate,



produced either by the action of potassium hydroxide on a solution of ethyl picrate in methyl alcohol or one of methyl picrate in ethyl alcohol, when decomposed by dilute sulphuric acid regenerates a mixture of the two alkyl picrates.

Potassium 3 : 5-dinitro-4-ethoxy-4-isobutylquinolnitrolate, produced by the action of potassium hydroxide on isobutyl picrate and ethyl alcohol or ethyl picrate and isobutyl alcohol, also yields a mixture of the two alkyl picrates on treatment with dilute sulphuric acid.

G. T. M.

**Nitro-derivatives of Phenanthraquinone and of Phenanthraquinol.** By JULIUS SCHMIDT and ADOLF KÄMPF (*Ber.*, 1902, **35**, 3117—3128).—3-Nitrophenanthraquinone is most readily prepared by the oxidation of 3-nitrophenanthrene (this vol., i, 29) with an acetic acid solution of chromic acid. It melts and decomposes at 279—280° (compare Schwabacher and Werner, this vol., i, 440) and may be crystallised from concentrated nitric acid. The nitro-derivative described by G. A. Schmidt as melting at 263° is undoubtedly impure (*Abstr.*, 1879, i, 941). 3-Nitrophenanthraquinonemono-oxime crystallises from benzene in yellow needles melting at 240°. Nitrodiphenylenequin-  
oxaline,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{C:N} > \text{C}_6\text{H}_4 \cdot \text{C:N}$ , obtained by the action of o-phenyl-

enediamine hydrochloride on 3-nitrophenanthraquinone, crystallises in greenish-yellow needles melting at 252—253°. Anschütz's 10-bromonitrophenanthrene (*Ber.*, 1878, **11**, 1218) does not contain the nitro-group in position 3.

Hot fuming nitric acid converts phenanthraquinone into 2 : 7-dinitrophenanthraquinone melting at about 300° and an isomeric dinitro-derivative melting at 215—217°, and more readily soluble in acetic acid than the 2 : 7-dinitro-compound.

Phenanthraquinone and its nitro-derivatives are readily reduced to the corresponding quinols by the action of an alcoholic solution of phenylhydrazine acetate or of hydrogen sulphide. Phenanthraquinol, (9 : 10-dihydroxyphenanthrene) melts sharply at 147—148° after sintering at 130° and yields a diacetyl derivative melting at 202°. 3-Nitro-9 : 10-dihydroxyphenanthrene crystallises in rose-red needles with a bluish lustre, melts at 222—223°, and dissolves in alkalis to deep indigo-blue solutions which rapidly absorb atmospheric oxygen. Its monoacetyl derivative crystallises in yellow needles melting and decomposing at 234—235°.

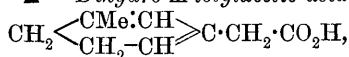
2 : 7-Dinitro-9 : 10-dihydroxyphenanthrene crystallises from alcohol in minute, brick-red needles melting and decomposing at 274°. It dissolves in sodium hydroxide, yielding a green solution which absorbs oxygen but slowly. The monobenzoyl derivative,  $\text{C}_{24}\text{H}_{12}\text{O}_7\text{N}_2$ , forms a yellow powder which sinters at 260° and is completely melted at 271°. The diacetyl derivative,  $\text{C}_{18}\text{H}_{12}\text{O}_8\text{N}_2$ , crystallises in pale yellow

needles melting and decomposing at  $285^{\circ}$ ; on reduction, it yields a stable diamino-compound which, after diazotising, can be used for the preparation of sparingly soluble azo-dyes.

An isomeric *dinitro-9:10-dihydroxyphenanthrene*\* may be obtained by reducing the dinitrophenanthraquinone of unknown constitution with hydrogen sulphide; it crystallises in glistening, pale-red plates melting at  $201^{\circ}$ . Its *dibenzoyl* derivative melts at about  $210^{\circ}$  and its *diacetyl* derivative at  $258^{\circ}$ .  
J. J. S.

**Enantiomorphic Structure of some Compounds of Camphor revealed by Etching. Resolution of Racemic Benzylidene Camphor. Isomorphism of its Active Components.** By JULES MINGUIN (*Bull. Soc. Chim.*, 1902, [iii], 27, 888—892).—The crystals of the camphor compounds have a completely symmetrical form, although in solution they are optically active. The author demonstrates, in the case of benzylidenecamphor and *p*-bromobenzylidenecamphor, that the corrosion figures obtained by means of benzene exhibit enantiomorphism. The author has also found that the enantiomorphic forms of benzylidenecamphor can give mixed crystals, so that the crystals of the one form can induce the crystallisation of the other. The author puts forward the idea that pseudo-racemism, and even true racemism, may be due entirely to the relative arrangement of the crystalline molecules of the oppositely active forms.  
A. F.

**Terpenes and the Ethereal Oils.** By OTTO WALLACH (*Annalen*, 1902, 323, 135—160. Compare Abstr., 1901, i, 155—157).—[With HANS BÖTTCHER.]— $\Delta^{1:5}$ -*Dihydro-m-tolylacetic acid*,



resulting from the hydrolysis of its ethyl ester with sodium methoxide, crystallises from alcohol in needles melting at  $170$ — $172^{\circ}$ ; the *amide* melts at  $146$ — $147^{\circ}$ . The ester itself was not obtained pure, but is produced by condensing methylcyclohexenone with ethyl bromoacetate in the presence of zinc. The unsaturated acid yields dihydro-xylene when heated for 5 hours at  $160^{\circ}$ .

*Ethyl*  $\Delta^{1:5}$ -*dihydro-3:5-xylyl-1-acetate* (or *3:5-dimethyl- $\Delta^{1:5}$ -dihydro-phenylacetate*),  $\text{CH}_2 \begin{array}{c} \text{CMe} = \text{CH} \\ \text{CHMe} \cdot \text{CH} \end{array} \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , prepared by condensing *3:5-dimethylcyclohexenone* with ethyl bromoacetate, boils at  $136$ — $137^{\circ}$  under 18 mm. pressure; the *acid*, produced by hydrolysing the ester with sodium ethoxide and acidifying the product, crystallises from acetone or methyl alcohol in yellow flakes, melts at  $150$ — $152^{\circ}$ , and boils at  $170^{\circ}$  under 15 mm. pressure; the *amide* melts at  $126$ — $127^{\circ}$ . The two unsaturated acids are also characterised by their *silver* salts.

*3:5-Dimethyl- $\Delta^{1:5}$ -dihydrophenylacetic acid*, when heated in closed tubes at  $200^{\circ}$ , yields  $\Delta^{1:5}$ -*dihydromesitylene*, which boils at  $147^{\circ}$  under the ordinary pressure and has a sp. gr. 0.826 at  $18^{\circ}$ . When the unsaturated acid is distilled with soda-lime, it yields a mixture of this hydrocarbon and mesitylene.

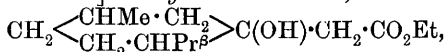
*Ethyl propylidenebisacetoacetate*, prepared by mixing propaldehyde with ethyl acetoacetate and slowly adding diethylamine to the mixture,



crystallises from alcohol in silky needles melting at 76—78°; when heated with potassium hydroxide solution, it gives rise to 3-methyl-5-ethyl- $\Delta^2$ -cyclohexenone, a substance boiling at 102° under 14 mm. pressure and 232° under the ordinary pressure. This ketone, when condensed with ethyl bromoacetate, yields ethyl 5-methyl-3-ethyl- $\Delta^{1:5}$ -dihydro-phenylacetate,  $\text{CH}_2 \begin{smallmatrix} \text{CMe}=\text{CH} \\ \text{CHEt}\cdot\text{CH} \end{smallmatrix} \gg \text{C}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , from which the free unsaturated acid is obtained by hydrolysis with alkalis; the ester boils at 145—147° under diminished pressure, the acid melts at 141—143° and yields a *silver* salt and an *amide*, the latter melting at 123°. When heated in closed tubes at 200°, the acid yields a mixture of *s*-dimethylethylbenzene and a *hydrocarbon*,  $\text{C}_{10}\text{H}_{16}$ , boiling at 166—172° and having a sp. gr. 0.0834 at 20°; the latter substance is unsaturated, but does not furnish a solid nitrosochloride or nitrosite.

3-Methyl-5-isopropyl- $\Delta^2$ -cyclohexenone is most conveniently condensed with ethyl bromoacetate by adding zinc turnings to the warm mixture diluted with benzene; the *ester*,  $\text{C}_{14}\text{H}_{20}\text{O}_2$ , thus produced boils at 154—158° under 16 mm. pressure and has the composition of an aromatic derivative; the corresponding *acid*,  $\text{C}_{12}\text{H}_{16}\text{O}_2$ , does not melt sharply, one portion fusing at 111—114° and another at 135—140°. The two fractions, however, have the same percentage composition. When heated at 200°, the acid yields a *hydrocarbon* boiling at 186—194° and having the properties of a *dimethylisopropylbenzene*,  $\text{C}_{11}\text{H}_{16}$ .

[With FRITZ THÖLKE.]—Ethyl mentholacetate,



produced by condensing menthone with ethyl bromoacetate, boils at 150—152° under 14 mm. pressure and possesses an odour of cedar oil; the corresponding acid yields a well-defined *silver* salt. The *unsaturated ester*,  $\text{CH}_2 \begin{smallmatrix} \text{CHMe}\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CHPr}^\beta \end{smallmatrix} \gg \text{C}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , results from the action of potassium hydrogen sulphate on the preceding ester at 140—150°; it boils at 140—142° under 14 mm. pressure; the *unsaturated acid* boils at 158—163° under 10 mm. pressure and is characterised by means of its *silver* salt. *Homomenthene*,  $\text{C}_{11}\text{H}_{20}$ , obtained by heating the unsaturated acid under pressure at 270—280°, boils at 186—187° under the ordinary pressure and has a sp. gr. 0.8215 and  $n_D$  1.4579 at 23°. The *hydrocarbon* is probably 1:5-dimethyl-2-ethyl- $\Delta^1$ -tetrahydrobenzene.

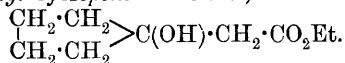
*Ethyl carvomentholacetate*,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2\cdot\text{CHMe} \\ \text{CHPr}^\beta\cdot\text{CH}_2 \end{smallmatrix} \gg \text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , produced from carvomenthone by the general method, boils at 162—164° under 16 mm. pressure and possesses the odour of cedar oil; the corresponding acid yields a *silver* salt,  $\text{C}_{12}\text{H}_{21}\text{O}_3\text{Ag}$ ; the *unsaturated ester* boils at 150—152° under 13 mm. pressure, and the corresponding *acid* at 166—172° under 11 mm. pressure.

*Homocarvomenthene*,  $\text{C}_{11}\text{H}_{20}$ , obtained by heating the unsaturated acid, boils at 194—196° under the ordinary pressure and has a sp. gr. 0.8300 and  $n_D$  1.46187 at 20°.

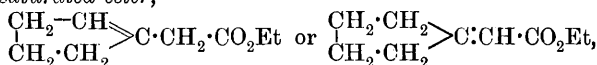
The condensation of carvenone with ethyl bromoacetate leads to the

formation of an *unsaturated ester*,  $C_{14}H_{22}O_2$ , boiling at  $135-137^\circ$  under 16 mm. pressure: the *unsaturated acid* boils at  $175-180^\circ$  under 17 mm. pressure with slight decomposition; it yields a *silver salt*,  $C_{12}H_{17}O_2Ag$ . A *hydrocarbon*,  $C_{11}H_{18}$ , produced on heating the *unsaturated acid* at  $250-260^\circ$ , boils at  $194-197^\circ$  under the ordinary pressure and has a sp. gr. 0.851 and  $n_D$  1.4821 at  $22^\circ$ . Homolimonene is analogous with the preceding compound and is obtained in the ordinary way from ethyl dihydrocarveolacetate (Abstr., 1901, i, 156); it boils at  $191-192^\circ$  and has a sp. gr. 0.8465 and  $n_D$  1.4771 at  $20^\circ$ .

[With NICOLAI SPERANSKI.]—When condensed with ethyl bromoacetate, pentanone yields an oily product boiling at  $105-107^\circ$  under 11 mm. pressure which, although not obtained in a state of purity, is considered to be *ethyl cyclopentanolacetate*,



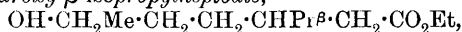
The *unsaturated ester*,



produced by heating the preceding compound with potassium hydrogen sulphate at  $130^\circ$ , is an oil boiling at  $82-84^\circ$  under 11 mm. pressure; the corresponding *acid*,  $C_7H_{10}O_2$ , boils at  $122^\circ$  under this pressure and melts at  $49-50^\circ$ ; its  *dibromide*,  $C_7H_{10}O_2Br_2$ , melts at  $88^\circ$  and its *amide*,  $C_7H_9 \cdot \text{CO} \cdot \text{NH}_2$ , at  $144^\circ$ . On oxidation with chromic acid in glacial acetic acid solution, the preceding acid yields a small amount of pentanone.

G. T. M.

**Terpenes and Ethereal Oils.** **Tetrahydrocarvoneisooxime.** By OTTO WALLACH (*Annalen*, 1902, 323, 323—333. Compare Abstr., 1900, i, 590).—[With L. FRESSENIUS.]—Tetrahydrocarvoneisooxime (m. p.  $104^\circ$ ), obtained by the transformation of tetrahydrocarvone-oxime, yields a crystalline hydrochloride,  $C_{10}H_{19}NO \cdot HCl$ ; this substance is, however, only produced in ethereal solution and is dissociated by water. The amino-acid (m. p.  $201-202^\circ$ ), produced from the *isooxime* by ring fission, is now shown to be  $\epsilon$ -amino- $\beta$ -isopropylheptonic acid,  $\text{NH}_2 \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHPr}^\beta \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ ; its *ethyl ester* is a colourless, odourless liquid boiling at  $149^\circ$  under 20 mm. pressure; the *methyl ester* boils at  $133-134^\circ$  under 18 mm. pressure. When treated with sodium nitrite and acetic acid, the preceding ethyl ester gives rise to a mixture of *ethyl decenoate*,  $\text{CHMe} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CHPr}^\beta \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , and *ethyl  $\epsilon$ -hydroxy- $\beta$ -isopropylheptate*,



the former of these boiling at  $108-111^\circ$  and the latter at  $152-155^\circ$  under 13 mm. pressure.

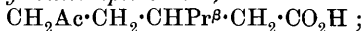
Ethyl  $\epsilon$ -amino- $\beta$ -isopropylheptate combines with methyl iodide yielding the quaternary iodide,  $C_{10}H_{18}O_2\text{Et} \cdot \text{NMe}_3\text{I}$ ; the substance, when treated with silver chloride, forms a hygroscopic chloride which is identified in the form of its *platinichloride*,  $C_{30}H_{62}O_4N_2 \cdot H_2PtCl_6$ .

The corresponding betaine,  $\text{CHMe} \begin{array}{c} \text{CH}_2 - \text{CH}_2 \cdot \text{CHPr}^\beta \\ | \\ \text{NMe}_3 \cdot \text{CO}_2 \cdot \text{CH}_2 \end{array}$ , obtained by

treating the quaternary iodide with silver oxide, is an amorphous, hygroscopic substance which yields a *platinichloride*,



The  $\epsilon$ -amino-acid, when treated with nitrous acid, yields a mixture of three substances, a lactone, an unsaturated acid, and a hydroxy-acid. The first two only are volatile in steam. The non-volatile product is a viscid, non-crystallisable substance which yields a ketonic acid, probably  $\beta$ -isopropyl- $\epsilon$ -ketoheptoic acid,



this compound melts at  $37-38^\circ$  and forms a semicarbazone melting at  $151-152^\circ$  (compare Baeyer and Villiger, Abstr., 1900, i, 133). On further oxidation, the hydroxy-acid gives rise to isopropylglutaric acid.

The lactone,  $\text{CHMe}\langle\begin{smallmatrix}\text{CH}_2-\text{CH}_2\\ \text{O}\cdot\text{C}\cdot\text{O}\cdot\text{CH}_2\end{smallmatrix}\rangle\text{CHPr}^\beta$ , is identical with the substance obtained by oxidising tetrahydrocarvone (Baeyer and Villiger, *loc. cit.*).

The unsaturated compound is a decenoic acid (Abstr., 1901, i, 590) having the formula  $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CHPr}^\beta\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ; the *amide* melts at  $63-64^\circ$  and on treatment with phosphoric oxide yields the nitrile,  $\text{C}_9\text{H}_{17}\text{CN}$ , a substance boiling at  $99-100^\circ$  under 12 mm. pressure. A base boiling at  $89-90^\circ$  under 12 mm. pressure is obtained by reducing the nitrile with sodium and alcohol; it yields an alcohol on treatment with nitrous acid. G. T. M.

**Terpenes and Ethereal Oils.** Compounds of the Thujone Series. By OTTO WALLACH (*Annalen*, 1902, 323, 333-373. Compare Abstr., 1895, i, 619; 1897, i, 246).—*iso*Thujone, when oxidised with potassium permanganate solution, gives rise to a ketolactone and two acids.

The ketolactone,  $\text{C}_{10}\text{H}_{16}\text{O}_3$ , melts at  $43-44^\circ$  and yields a *semicarbazone*,  $\text{C}_{10}\text{H}_{16}\text{O}_2\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , melting at  $188-189^\circ$ .

The *oxime*,  $\text{C}_{10}\text{H}_{16}\text{O}_2\cdot\text{NOH}$ , separates from dilute methyl alcohol in transparent, prismatic crystals melting at  $155-156^\circ$ ; the *phenylhydrazone* forms snow-white crystals and melts at  $144-146^\circ$ .

The ketolactone is not identical with that obtained from thujamenthone.

The acidic products of the oxidation of *isothujone* are ketonic acids having the formulæ  $\text{C}_8\text{H}_{14}\text{O}_3$  and  $\text{C}_9\text{H}_{16}\text{O}_3$ , and are separated by the fractional crystallisation of their semicarbazones in alcohol.

The semicarbazone of the former acid melts at  $188-189^\circ$ ; and acid regenerated from this derivative melts at  $73-74^\circ$ , boils at  $145^\circ$  under 10 mm. pressure, and when oxidised with sodium hypobromite decomposes into bromoform and isopropylsuccinic acid. This result indicates that the  $\text{C}_8$  acid is an *isopropylævulvic acid* having one of the following formulæ,  $\text{CH}_2\text{Ac}\cdot\text{CHPr}^\beta\cdot\text{CO}_2\text{H}$  or  $\text{CHAcPr}^\beta\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .

This acid yields an *oxime*,  $\text{C}_8\text{H}_{14}\text{O}_2\cdot\text{NOH}$ , melting at  $119-120^\circ$  and a *phenylhydrazone* melting at  $100-101^\circ$ .

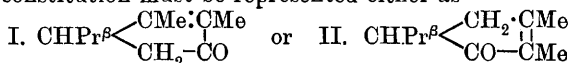
The other ketonic acid,  $\text{C}_9\text{H}_{16}\text{O}_3$ , is an odourless liquid boiling at  $158^\circ$  under 11 mm. pressure; its *semicarbazone* is readily soluble in hot alcohol and boils at  $154-156^\circ$ ; the *oxime* melts at  $77^\circ$ . On oxidation

with potassium hypobromite, the ketonic acid yields a lactone and a dibasic acid melting at 106—108° which is probably *isopropylsuccinic acid*.

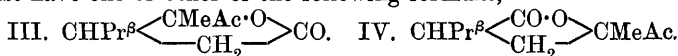
The ketolactone, when oxidised with permanganate, nitric acid, or sodium hypobromite, gives rise to an *acid*,  $C_9H_{14}O_4$ , which is isomeric with homoterpenylic acid and resembles this substance by crystallising with  $1H_2O$ ; it crystallises from dilute methyl alcohol in plates melting at 52·5—53·5° and boils at 205—206° under 12 mm. pressure; its *silver salt*,  $C_9H_{13}O_4Ag$ , is soluble. When the oxidation is carried further by means of chromic acid, the preceding acid yields *isopropyl-lævulic acid*.

*Benzylideneisothujone*,  $C_{10}H_{14}O:CHPh$ , results from the interaction of benzaldehyde and *isothujone* in the presence of an alcoholic solution of sodium ethoxide; it boils at 210—212° under 12 mm. pressure and melts at 83°.

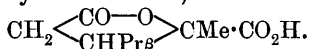
Since *isothujone* can be ultimately oxidised to an *isopropyllævulic acid*, its constitution must be represented either as



according as to whether the *isopropyl* group in the oxidation product is in an  $\alpha$ - or a  $\beta$ -position. Assuming that Wagner's rule for the oxidation of ethylene derivatives holds in this case, the ketolactone must have one or other of the following formulæ,



The condensation with benzaldehyde indicates that *isothujone* contains the residue  $CO \cdot CH_2$ , and accordingly formula I is to be preferred for the ketone. From this, the ketolactone should be represented by formula III, the acid  $C_9H_{14}O_4$  being therefore represented by



The constitution of the acid  $C_9H_{16}O_3$  is still uncertain.

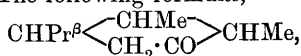
Thujamenthylamine,  $C_{10}H_{19} \cdot NH_2$ , the base obtained by reducing the oxime of thujamenthone, boils at 198—200° under the ordinary pressure and has a sp. gr. 0·8095 and  $n_D$  1·4531. It yields *acetyl* and *benzoyl* derivatives and a *carbamide* and *phenylthiocarbamide*, these substances melting at 128—129°, 106—107°, 205—206° and 112° respectively; the *phenylcarbamide* is amorphous and the *hydrochloride* is crystalline.

*Benzylidenethujamenthone*,  $C_{10}H_{16}O:CHPh$ , produced by condensing *isothujone* with benzaldehyde, boils at 180—182° under 11 mm. pressure but does not crystallise.

Thujamenthoketonic acid,  $C_{10}H_{18}O_3$ , the oxidation product of thujamenthone, yields a *silver salt* and a *semicarbazone*,  $C_{11}H_{21}O_3N_3$ , which melts somewhat indefinitely at 170—175° and is soluble in ammonia. The ketonic acid, on oxidation with sodium hypobromite, gives rise to a dibasic acid,  $C_9H_{16}O_4$ , which melts at 137—138° and crystallises from ether in transparent prisms; the *silver salt* has the composition  $C_9H_{14}O_4Ag_2$ .

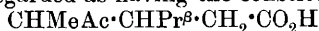
The oxidation of thujamenthone also results in the formation of a ketolactone,  $C_{10}H_{16}O_3$ ; this product crystallises from ether, melts at 42°, and boils at 130—132° under 10 mm. pressure; the *oxime* melts at

158—159°. The *semicarbazone* crystallises in needles and melts at 179—180°; the *phenylhydrazone* forms white leaflets melting at 144—146°. The ketolactone closely resembles the corresponding substance derived from *isothujone*, and the two compounds yield semicarbazones, oximes, and phenylhydrazones which are very similar. The greatest difference is observed in their products of oxidation; the ketolactone from *isothujone* gives a dibasic acid crystallising with 1H<sub>2</sub>O and melting at 52—53°, whilst the ketolactone from *thujamenthone* yields an isomeric lactone-acid, C<sub>9</sub>H<sub>14</sub>O<sub>4</sub>, which is anhydrous and melts at 94°; the product, on further oxidation, gives rise to *isopropyllævulic* acid. The following formulæ,



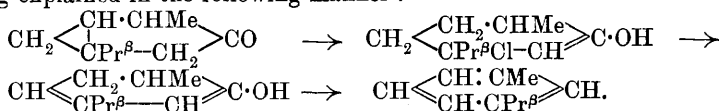
$\text{CHPr}^\beta \begin{array}{c} \text{CMeAc} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CO} \end{array} \text{O}, \text{CH}_2 \begin{array}{c} \text{CO} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{CHPr}^\beta \end{array} \text{CMe} \cdot \text{CO}_2\text{H}$ , are suggested for *thujamenthone*, the ketolactone, and the lactone-acid respectively.

*Thujamenthoketonic* acid and the dibasic acid ( $\alpha$ -methyl- $\beta$ -isopropylglutaric acid?) are regarded as having the constitutions



and  $\text{CO}_2\text{H} \cdot \text{CHMe} \cdot \text{CHPr}^\beta \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$  respectively.

The formula for *thujone* suggested by Semmler (compare Abstr., 1893, 107; 1896, 330; 1897, i, 247) is confirmed by the observation that this ketone, when saturated with hydrogen chloride and heated at 120—150°, gives rise to a considerable quantity of *cymene*, the reaction being explained in the following manner:



The substance *dihydrocarvacrol*, represented by the third formula, is probably produced by the action of ferric chloride on *thujone* and under these conditions becomes oxidised to *carvacrol*.

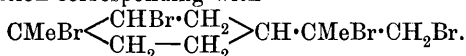
The above formula for *thujone* does not, however, explain the formation of *tanacetogenic* acid and *camphoric* acid (m. p. 146°) from this ketone by the action of sodium hypobromite. G. T. M.

**Terpenes and Ethereal Oils: Terpeneol.** By OTTO WALLACH and O. RAHN (*Annalen*, 1902, 324, 79—97. Compare Abstr., 1895, i, 547; Tiemann and Semmler, *ibid*, i, 548).—1 : 8 : 9-*Tribromoterpane*,

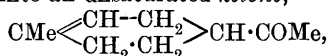
$\text{CMeBr} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{CH} \cdot \text{CMeBr} \cdot \text{CH}_2\text{Br}$ , prepared by adding successively bromine and hydrogen bromide to a glacial acetic acid solution of Helle and Stephan's terpeneol (compare this vol., i, 641), crystallises from dilute alcohol and melts at 67°. When treated with 1 mol. of bromine, the tribromide yields *dipentene tetrabromide* melting at 123°.

The *monobromide*, C<sub>10</sub>H<sub>15</sub>Br, produced by treating the tribromide with sodium methoxide in methyl alcohol solution, is an oily substance boiling at 105—110° under 10 mm. pressure, and yielding with bromine a *pentabromide*, which separates from alcohol or ethyl acetate in white crystals and melts at 137°. Assuming that the removal of bromine

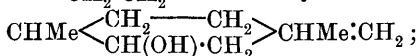
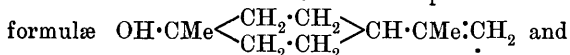
by sodium methoxide takes place in the same way as in the case of dipentene tetrabromide, the monobromide may be represented by the formula  $\text{CMe} \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{CMe} \cdot \text{CHBr}$ , whilst the pentabromide has a constitution corresponding with



Helle and Stephan's terpineol yields 1 : 8 : 9-trihydroxyterpane (m. p.  $118^\circ$ ), and this in turn gives rise to the ketone  $\text{C}_9\text{H}_{12}\text{O}_2$ . When warmed with dilute sulphuric acid, the latter product loses water, and becomes converted into an unsaturated ketone,

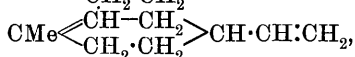


isomeric with phorone, which boils at  $205-206^\circ$  and has a sp. gr. 0.940 and  $n_D$  1.4719 at  $19^\circ$ . The *semicarbazone* crystallises from alcohol in lustrous leaflets melting at  $164-165^\circ$ , the *oxime* melts at  $51^\circ$ , and on treatment with bromine yields the *dibromo-oxime* decomposing at  $150^\circ$ . The unsaturated ketone is a *p*-acetyltetrahydrotoluene, for when heated with concentrated sulphuric acid it loses hydrogen and furnishes *p*-acetyltoluene. The terpineol melting at  $32^\circ$  and dihydrocarveol are isomeric substances represented respectively by the formulæ

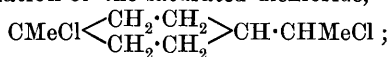


the latter compound yields successively a trihydroxyterpane, the hydroxyketone,  $\text{CHMe} \begin{smallmatrix} \text{CH}_2 - \text{CH}_2 \\ \text{CH}(\text{OH}) \cdot \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{COMe}$ , and the above-mentioned *p*-acetyltetrahydrotoluene; the final product, when reduced with sodium in dilute alcoholic or ethereal solution, gives rise to the terpineol,  $\text{CMe} \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{CHMe} \cdot \text{OH}$ , which boils at  $212-213^\circ$ , and has a sp. gr. 0.942 and  $n_D$  1.4836 at  $19^\circ$ ; its *phenylurethane* crystallises from dilute methyl alcohol and melts at  $69^\circ$ . This alcohol, which is a lower homologue of the terpineol melting at  $35^\circ$ , when heated either with dilute solutions of oxalic or sulphuric acid or with sodium hydrogen sulphate at  $180-190^\circ$ , becomes converted into a lower homologue of cineol; this product boils at  $168-172^\circ$ , has a sp. gr. 0.92, and shows the characters of a saturated *oxide*,  $\text{C}_9\text{H}_{16}\text{O}$ , being stable towards potassium permanganate solution.

A *hydrocarbon*,  $\text{CMe} \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{C} \cdot \text{CHMe}$  or



is obtained from the secondary alcohol by saturating its chloroform solution with hydrogen chloride and adding phosphorus pentachloride; it boils at  $160-163^\circ$ , and has a sp. gr. 0.843 and  $n_D$  1.47586 at  $22^\circ$ . The action of hydrogen chloride and phosphorus pentachloride probably results in the formation of the saturated dichloride,



this product, by the loss of hydrogen chloride, would furnish a hydrocarbon having one or other of the formulæ just given. G. T. M.

**Terpenes and Ethereal Oils :** Trimethylcyclohexenone, Trimethylcyclohexanone, and 3:3-Dimethylcyclopentanone. By OTTO WALLACH and A. SCHEUNERT (*Annalen*, 1902, 324, 97—112).—*a*-cyclo-Geraniolene, the chief product of the transformation of geraniolene, yields a nitrosochloride melting at 100—120° and a nitrosate,  $C_9H_{16}O_4N_2$ , melting at 102—104°. The corresponding nitrolepiperidide,

$$\begin{array}{c} C_9H_{16}ON \cdot C_5NH_{10} \\ C_9H_{16}ON \cdot NH \cdot CHPh \end{array}$$
and nitrobenzylamine, melt respectively at 136—138° and 106°.

2:4:4-Trimethylcyclo- $\Delta^2$ -hexenoneoxime, resulting from the action of alcoholic alkali hydroxides on the nitrosochloride or the nitrosate, boils at 131—132° under 15 mm. pressure and crystallises in prisms melting at 128—129°.

2:4:4-Trimethylcyclo- $\Delta^2$ -hexenone,  $CM_e_2 \begin{array}{c} CH \cdot CM_e \\ CH_2 \cdot CH_2 \end{array} CO$ , produced by hydrolysing the preceding compound with dilute sulphuric acid, is a colourless liquid boiling at 195—196° and having an odour resembling that of tanacetol; it has a sp. gr. 0.9245 and  $n_D$  1.4749 at 25°; the molecular refraction, deduced from experiment, is 42.02, whilst the calculated value for an unsaturated alcohol containing two ethylene linkings is 42.16. Accordingly, the ketone appears to exist in the enolic form.

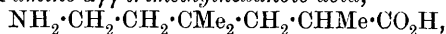
The semicarbazone,  $C_9H_{14}N \cdot NH \cdot CO \cdot NH_2$ , melts at 158—159°; the benzylidene derivative,  $CHPh : C \begin{array}{c} CO - CM_e \\ CH_2 \cdot CM_e \end{array} CH$ , obtained by condensing the ketone with benzaldehyde in the presence of sodium ethoxide, melts at 54—55°.

2:4:4-Trimethylcyclohexanol,  $CM_e_2 \begin{array}{c} CH_2 \cdot CHMe \\ CH_2 - CH_2 \end{array} CH \cdot OH$ , results from the reduction of the unsaturated ketone with sodium in ethereal or alcoholic solution; in the former case, a considerable amount of pinacone is produced. The saturated alcohol is a viscid, colourless oil boiling at 192—193° and has a camphor-like odour.

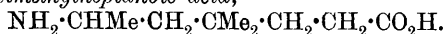
2:4:4-Trimethylcyclohexanone,  $CM_e_2 \begin{array}{c} CH_2 \cdot CHMe \\ CH_2 - CH_2 \end{array} CO$ , obtained by oxidising the preceding alcohol with chromic acid, boils at 191° and has a sp. gr. 0.902 and  $n_D$  1.4545 at 19°; its semicarbazone,  $C_9H_{16}N \cdot NH \cdot CO \cdot NH_2$ , and oxime melt respectively at 164—165° and 108—109°. The latter derivative, when treated with moderately concentrated sulphuric acid, becomes transformed into the isooxime melting at 115—116°; this product, when saturated with hydrogen chloride in ethereal solution, yields a stable hydrochloride. The isooxime should have one or other of the formulæ

$$CHMe \begin{array}{c} CH_2 \cdot CM_e \cdot CH_2 \\ CO \cdot NH - CH_2 \end{array}$$
and  $CHMe \begin{array}{c} CH_2 \cdot CM_e \cdot CH_2 \\ NH - CO - CH_2 \end{array}$ and, accordingly, the aminocarboxylic

acid obtained by its hydrolysis with 20 per cent. hydrochloric acid at 150° is either  $\epsilon$ -amino- $\gamma$ -trimethylhexanoic acid,

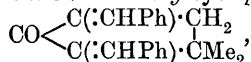


or  $\epsilon$ -amino- $\gamma$ -dimethylheptanoic acid,



This acid separates from dilute alcohol in colourless crystals melting at 160—161°.

The constitution of 2 : 4 : 4-trimethylcyclohexanone is determined by studying the products of its oxidation. *iso*Geronic acid results from the action of potassium permanganate and is identified by means of its semicarbazone. The ketonic acid, on treatment with potassium hypobromite, yields  $\beta\beta$ -dimethyladipic acid, which melts at 85—86° and is characterised by its silver salt and by conversion into 3 : 3-dimethylcyclopentanone,  $\text{CO} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CMe}_2 \end{smallmatrix}$ , through the agency of its calcium salt. This cyclic ketone, regenerated from its semicarbazone (m. p. 174—175°), boils at 154—155° and has the odour of menthone. The production of dibenzylidene-3 : 3-dimethylcyclopentanone,



by the action of 2 mols. of benzaldehyde on the ketone in the presence of sodium ethoxide proves that the methyl groups are not in an  $\alpha$ -position with respect to the carbonyl radicle.

The dibenzylidene derivative crystallises from ethyl acetate in brilliant, yellow needles and melts at 138—139°. Benzylidene- $\beta\beta$ -dimethylcyclopentanone, obtained from the ketone by the action of 1 mol. of benzaldehyde, is very soluble in alcohol or ether and separates from a mixture of the latter solvent and light petroleum in pale yellow crystals melting at 66—67°. G. T. M.

**Terpenes and Ethereal Oils.** Transformation of Cyclic Hydrocarbons and Ketones. By OTTO WALLACH and M. FRANKE (*Annalen*, 1902, 324, 112—117. Compare preceding abstract).—Dihydroisophorone, derived from isophorone (compare Knoevenagel, Abstr., 1897, i, 611), has a constitution corresponding with the formula  $\text{CHMe} \begin{smallmatrix} \text{CH}_2 - \text{CO} \\ | \\ \text{CH}_2 \cdot \text{CMe}_2 \end{smallmatrix} \text{CH}_2$ , and is therefore 3 : 5 : 5-trimethylcyclohexanone, differing only from 2 : 4 : 4-trimethylcyclohexanone, produced from cyclogeraniolene, in the position of its carbonyl group. The first of these isomerides can be transformed into the second by the following series of changes.

The crystalline *trans*-dihydroisophorol,  $\text{C}_9\text{H}_{17} \cdot \text{OH}$ , on treatment with phosphoric oxide or anhydrous zinc chloride, yields  $\alpha$ -cyclogeraniolene, and this hydrocarbon, when treated in the manner indicated in the preceding abstract, gives 2 : 4 : 4-trimethylcyclohexanone.

3-Methylcyclohexanol, when dehydrated with zinc chloride, gives rise to a tetrahydrotoluene,  $\text{C}_7\text{H}_{12}$ , which is isomeric with the hydrocarbon derived from methylcyclohexyl chloride. The new hydrocarbon yields a nitrosate, which, in turn, furnishes a methylcyclohexenone,  $\text{C}_7\text{H}_{10}\text{O}$ , differing in properties from 3-methylcyclohexanone (Knoevenagel, Abstr., 1897, i, 606). G. T. M.

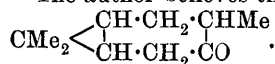


**Isomeric Changes in the Thujyl Series: Constitution of Thujone.** By IWAN L. KONDAKOFF (*Chem. Zeit.*, 1902, **26**, 720—724).—Thujyl alcohol, which is probably a dicyclic compound, is converted by phosphorus pentachloride into an unstable thujyl chloride of inconstant composition (compare Semmler, *Abstr.*, 1893, i, 178); it consists mainly of a tertiary compound which, with moist silver oxide, gives a tertiary alcohol, with bromine evolves hydrogen bromide, and with alcoholic potassium hydroxide forms a mixture of at least two hydrocarbons; these, in their properties, resemble, on the one hand, dicyclic thujene (Tschugaeff, *Abstr.*, 1901, i, 38) and the sabinenes, and on the other, monocyclic tanacetene (Semmler, *loc. cit.*) and Wallach's thujene (*Abstr.*, 1893, i, 105). From the hydrocarbon fraction (b. p. 160—175°), dipentene dihydrochloride can be obtained by treatment with hydrochloric acid. Thujyl chloride and hydrogen chloride yield two hydrochlorides, one of which is dipentene dihydrochloride. Thujone does not form an additive product with hydrogen chloride, but with hydrogen bromide gives a substance which boils at 105—117° under 11 mm. pressure; by moist silver oxide, it is converted into an optically inactive ketonic alcohol which boils at 229—231° under the ordinary pressure and at 105—106° under 11 mm. pressure, and has a sp. gr. 0.9314 at 20°, and  $n_D$  1.4841; its *oxime* melts at 114.5—115°.

By prolonged treatment, or by warming, with hydrochloric acid, thujyl chloride is converted into a *dichloride* which boils at 116—130° under 12 mm. pressure, and is heavier than water; it is perhaps identical with the dichloride of dihydrocarveol.

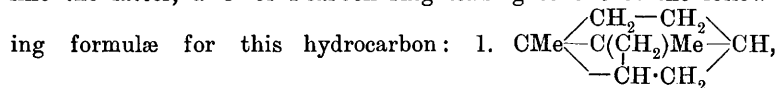
*Thujyl bromide* is prepared by the action of hydrogen bromide on thujyl alcohol; it boils at 110—117° under 11 mm. pressure and has a sp. gr. 1.007 at 20° and  $[\alpha]_D + 23.5'$ ; it appears to be a secondary compound.

The author believes that thujone is best represented by the formula



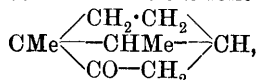
K. J. P. O.

**The Constitution of Camphene.** By FRANK D. DODGE (*J. Amer. Chem. Soc.*, 1902, **24**, 649).—When pinene and camphene are treated with acetic acid containing 1 per cent. of sulphuric acid, they are converted to the extent of 43 and 77 per cent. into terpineol and isobornyl acetates respectively, whilst limonene, terpinolene, and terpinene are, under the same conditions, esterified to the extent only of 4, 11, and 8 per cent. To account for this similarity in reaction of camphene and pinene, it is suggested that the former must contain, like the latter, a 3- or 4-carbon ring leading to one of the following formulæ for this hydrocarbon:



2.  $\text{CH}_2 \cdot \text{C} \begin{array}{l} \diagup \text{CH}_2 - \text{CH}_2 \\ \diagdown \text{CMe}_2 \\ \diagup \text{CH} - \text{CH}_2 \end{array} \text{CH}$ . The second of these would lead to a formula for camphenilone identical with that proposed by Wallach for

fenchocamphorone and is therefore improbable. The first formula represents camphene as a saturated substance which is in harmony with its behaviour to bromine and permanganate. It affords, further, an explanation of the formation of *isobornyl* acetate by the opening of the 4-carbon ring; the position of the latter, however, precludes any further rearrangement of the rest of the molecule such as occurs in the corresponding reaction with pinene and so accounts for the possibility of reobtaining camphene from *isoborneol*. Whilst the new formula is in agreement with the constitution assigned to camphoric acid, camphenylic acid, and camphene glycol, it is not in harmony with Jagelki's formula for camphenilone (Abstr., 1900, i, 627). This, since it assumes the presence of an oxidised 4-carbon ring is improbable and it is proposed to substitute for it the following formula



representing camphenilone as a true lower homologue of camphor and satisfactorily accounting for its principal reactions. If the presence of a 4-carbon ring in camphene be admitted, the symmetry of the camphor molecule suggests the possible occurrence of such 4-carbon rings in other positions and the reactions of camphenone would be satisfactorily

accounted for by the following formula:  $\text{CH} \begin{array}{c} \swarrow \text{CH}_2\text{---CH}_2 \\ \text{---C(CH}_2\text{)Me---} \\ \searrow \text{CH---CO} \end{array} \text{CMe},$

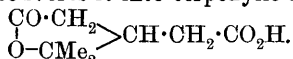
whilst fenchene, which reacts like pinene and camphene with acetic

acid, would be represented thus:  $\text{CH} \begin{array}{c} \swarrow \text{CH}_2\text{---CH}_2 \\ \text{---C(CH}_2\text{)Me---} \\ \searrow \text{CH---CHMe} \end{array} \text{CH}.$  This

formula, however, is not in harmony with Wallach's representation of fenchocamphorone (Abstr., 1900, i, 241). T. A. H.

**Oxidations with Mercuric Acetate.** By LUIGI BALBIANO and VINCENZO PAOLINI (*Ber.*, 1902, 35, 2994—2998; *Atti R. Accad. Lincei*, 1902, [v], 11, ii, 65—69. Compare Abstr., 1902, ii, 109).—Mercuric acetate reacts with olefines at the ordinary temperature, insoluble mercurous acetate being formed, along with acetic acid and oxidation products of the olefine.

*l*-Pinene is thus converted into *dioxypinene*,  $\text{C}_{10}\text{H}_{16}\text{O}_2$ , which is a viscid oil of sp. gr. 1.069 at 0°, boils at 145° under 4 mm. and at 170—171° under 20 mm. pressure, and is optically inactive. This substance behaves as a ketonic alcohol containing an ethylene linking; it combines with two atomic proportions of bromine and yields an *oxime* melting at 138.5°, which also unites with bromine, and a *semicarbazone* which crystallises in needles melting at 180°. The compound, with phenylcarbimide, crystallises in prisms melting at 125°. Oxidation with permanganate converts it into terpenylic acid,



[With A. NARDACCI].—Anethole is converted by mercuric acetate into a *glycol*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}_3\text{H}_5(\text{OH})_2$ , which crystallises in mammillary

groups of needles and melts at 98°. The *diacetyl* derivative is an oil which boils at 210° under 41 mm. pressure. The glycol is oxidised by chromic acid to anisic acid.

[With E. LUZZI].—*iso*Safrole, which contains the propenyl group, is readily oxidised by mercuric acetate, but the corresponding glycol has not yet been obtained pure. Safrole, on the other hand, which contains the allyl group, is not oxidised, but when treated with the acetate for four months yields a compound,  $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:C}_3\text{H}_5(\text{OH})\cdot\text{Hg}\cdot\text{OAc}$ , which forms crystalline crusts. An isomeric compound is obtained as a pale yellow syrup by the action of mercuric acetate for only 8–10 days. Both compounds, when treated with acids, yield safrole. Camphene behaves in a similar manner to safrole, yielding a crystalline mercury compound of complex constitution. A. H.

**Essential Oil of Asarum Arifolium.** By EMERSON R. MILLER (*Arch. Pharm.*, 1902, 240, 371–385).—By distilling the roots of *Asarum arifolium* with steam, shaking the oil with aqueous potassium hydroxide, fractionating the residual oil, and examining the various fractions, the following constituents were detected: *l*-pinene, eugenol, a phenol of unknown composition, methyleugenol, methylisoeugenol, safrole (the chief constituent), asarone, and probably a sesquiterpene. C. F. B.

**Constituents of Calamus Oil. I.** By HERMANN THOMS and R. BECKSTROEM (*Ber.*, 1902, 35, 3187–3195. Compare Abstr., 1901, i, 396).—The fraction of oil used had a sp. gr. 1.0254 at 20°,  $n_D$  1.68° at 26° in a 2 cm. tube, and distilled between 272° and 340° under the ordinary pressure. It contained free *n*-heptioic acid and palmitic acid, eugenol, asarylaldehyde, of which the oxime was also prepared and analysed, and esters of acetic and palmitic acids. From the fractions of high boiling point of the saponified oil a solid substance was isolated which separated in needle-shaped crystals, was crystallised from alcohol, and melted at 168°; for this substance, which has been observed by Schimmel & Co. (Schimmel's, *Ber.*, Oct., 1899, 8) and by Soden and Rojahn (Abstr., 1901, i, 395), the name *calameon* is proposed. Subsequent addition to the oils of moist ether or light petroleum caused the separation of a considerable quantity of asarone from which asarylaldehyde and asaronic acid were prepared; the amount of asarone in the oil can be directly deduced from the Zeisel methyl number, for none of the other constituents contains a methoxy-group.

By the action of arsenic acid on the fractionated oil, a solid arsenate was produced from which, after removing the arsenic, a polymeride of asarone was isolated; this was obtained as a white powder, consisting of minute, clear, transparent prisms, which melts at 203°, and distils with much decomposition between 175° and 225° under 16 mm. pressure; it can be prepared directly from pure asarone by the action of arsenic acid. It yields the same oxidation products as, and is partially reconverted into, asarone when distilled; its molecular weight corresponds with that required for the formula  $(\text{C}_{12}\text{H}_{16}\text{O}_3)_3$ , and the name *para*-asarone is suggested for the compound. After removing the whole of the asarone by this method or by means of sulphuric acid, a residue

of hydrocarbon was left; the fractions of high boiling point contained a laevorotatory hydrocarbon,  $C_{15}H_{22}$ , which had a sp. gr. 0.9336 at  $22^\circ$ , and  $[\alpha]_D - 13.38^\circ$  at  $22^\circ$ , whilst the fractions of low boiling point gave a dextrorotatory hydrocarbon which had a sp. gr. 0.9330 at  $18^\circ$ , and  $[\alpha]_D + 13.83^\circ$  at  $18^\circ$ ; the hydrocarbon could also be directly isolated by dissolving the fraction of the oil in light petroleum, treating with dry hydrogen chloride which precipitates the asarone and converts the hydrocarbon into the hydrochloride,  $C_{15}H_{22}HCl$ , which remains in solution and is left as a liquid on evaporating the solution; from this the hydrogen chloride is removed by distillation in a vacuum. T. M. L.

**Calameon from Calamus Oil.** By HERMANN THOMS and R. BECKSTROEM (*Ber.*, 1902, 35, 3195—3200).—*Calameon*,  $C_{15}H_{26}O_2$ , separated from the fractions of high boiling point of calamus oil, forms glistening, hemihedral, orthorhombic crystals, melts at  $168^\circ$ , dissolves in 22 parts of cold alcohol, sublimes in glistening needles when heated, and has  $[\alpha]_D - 8.94^\circ$  at  $26^\circ$  in alcohol; it is not an acid, phenol, aldehyde, ketone, ester, alcohol, or phenol ether, is not attacked by sodium in alcoholic solution, but in ethereal solution yields a sodium derivative,  $C_{15}H_{25}O_2Na$ , which forms a white, sandy precipitate, decomposes and becomes brown at  $168^\circ$ , and when boiled with water is reconverted into calameon.

*Calameonic acid*,  $C_{15}H_{24}O_4 \cdot H_2O$ , prepared by oxidising calameon with permanganate, crystallises from much ether in stout prisms, and melts with liberation of gas at  $153^\circ$ ; the anhydrous substance crystallises from ether and melts at  $138^\circ$ . The ammonium salt,  $C_{15}H_{23}O_4NH_4 \cdot 1\frac{1}{2}H_2O$  melts at  $180^\circ$ . The calcium salt, with  $6H_2O$ , crystallises in glistening flakes. Carbon dioxide, and acetic and oxalic acids are also formed in small quantities in the oxidation.

Calameon combines additively with two atomic proportions of bromine, but the compound is not stable, loses water and hydrogen bromide, leaving an oil of the formula  $C_{15}H_{21}Br$ . By passing dry hydrogen chloride into an ethereal solution of calameon, a hydrochloride,  $C_{15}H_{26}O_2HCl$ , is formed, which separates in white, needle-shaped crystals, melts at  $119^\circ$ , and is reconverted into calameon when boiled with alcohol.

When warmed with 80 per cent. sulphuric acid, acetyl chloride, or benzoyl chloride, calameon loses  $2H_2O$  and leaves a hydrocarbon, *calamene*,  $C_{15}H_{22}$ ; this is a clear, refractive liquid, boils at  $144^\circ$  under 15.5 mm. pressure, has a sp. gr. 0.9324 at  $23^\circ$ , and  $[\alpha]_D - 11.31^\circ$  at  $26^\circ$ , is not reduced by metallic sodium, but combines with water when warmed with a mixture of sulphuric and acetic acids. By the action of bromine, a substitution product,  $C_{15}H_{21}Br$ , is obtained as a pale-yellow oil. Calamene gives a crystalline hydrochloride which melts at  $108^\circ$ . On oxidation, it is converted completely into acetic and oxalic acids. T. M. L.

**Oil of Milfoil.** By A. B. AUBERT (*J. Amer. Chem. Soc.*, 1902, 24, 778—780).—This essential oil is of a dark bluish-green colour, and possesses a pleasant odour. It has a sp. gr. 0.9217 at  $22^\circ$ ,  $n_D 1.506$  at  $20^\circ$ , is miscible with absolute alcohol, ether, xylene, or chloroform, but only partially soluble in 95 per cent. alcohol. It was separated

by distillation under reduced pressure into the following fractions, 170—190° (7 per cent.), 190—210° (17 per cent.), 210—220° (50 per cent.), 220—235° (9 per cent.), and above 235° (3 per cent.), leaving 14 per cent. of a dark coloured, waxy residue. The first fraction was slightly acid; it gave indications of the presence of a small amount of cineol (?) and of an aldehyde with an odour of cedar-wood.

The fraction 210—220° had at first a deep blue colour, but became light yellow when left in the dark. It consists principally of a substance having the composition  $C_{12}H_{20}$ , which is optically active, having a rotation  $-14.2^\circ$  in a 100 mm. tube,  $n_D$  1.492, and boils at  $254^\circ$  (uncorr.) under 754.8 mm. pressure. When treated with bromine, it evolves hydrogen bromide and is converted into a pitch-like resin. T. A. H.

**Chinese Oil of Neroli.** By JOHN C. UMNEY and C. T. BENNETT (*Pharm. J.*, 1902, [iv], 15, 146—147).—A sample of Chinese oil of neroli, said to have been obtained from *Citrus triptera*, had a yellowish-brown colour with a slight blue fluorescence, sp. gr. 0.850 at  $15^\circ$ , and optical rotation  $+35^\circ$  in a 10 cm. tube. It contained 4.79 per cent. of esters (calculated as linalyl acetate) and 21.41 per cent. of free alcohols (calculated as linalool). By distillation under the ordinary pressure, the following fractions were obtained: 170—175°, 30 per cent.; 175—180°, 14 per cent.; 180—185°, 21 per cent.; 185—190°, 7 per cent.; above 190°, 28 per cent. The chief constituents of the oil are limonene, camphene (?), linalool, linalyl acetate (traces), methyl anthranilate, and a paraffin hydrocarbon. E. G.

**Chemistry of India-rubber.** By CARL D. HARRIES (*Ber.*, 1902, 35, 3256—3266).—When gaseous nitrous acid is passed through a benzene solution of Para rubber, a green, colloidal precipitate of the nitrosite,  $(C_{10}H_{16}O_3N_2)_x$ , separates, which is insoluble in all the common solvents except pyridine and aniline, which appear to decompose it. When this is further treated in suspension in benzene with nitrous acid, it changes to a yellow nitrosite (*nitrosite b*) which is soluble in ethyl acetate, acetone, or alkali solution, reduces Fehling's solution and decomposes when heated at  $130^\circ$ ; from ebullioscopic measurements in acetone solution, its molecular weight has been found to be about 600 and its formula is  $C_{20}H_{30}O_{16}N_6$ . When oxidised with nitric acid, this nitrosite gives a dark yellow powder of the formula  $C_{20}H_{31}O_{14}N_5$ , oxalic acid, and an oil which appears to contain an aliphatic nitro-acid. When oxidised with permanganate, *nitrosite b* gives a mixture of fatty acids, principally oxalic and succinic.

When Para rubber is dissolved in moist benzene and a rapid current of unwashed nitrous acid is passed through the solution, another yellow powder is obtained, which has the formula  $C_{20}H_{30}O_{14}N_6$ , and is termed *nitrosite c*. This decomposes at about  $160^\circ$ , and on oxidation gives products similar to those obtained from *nitrosite b*.

Myrcene (from Bay oil) polymerises to a thick, greenish oil when heated for 4 hours at  $300^\circ$ . On subjecting the product to fractional distillation at a pressure of 13 mm., about a third passed over between  $160^\circ$  and  $200^\circ$ , and this was found to be *dimyrcene*. The undistilled residue consists of *polymyrcene*, which is soluble in benzene. By the action of nitrous acid on dimyrcene, a nitrosite is produced which is

apparently identical with *nitrosite c* obtained from rubber. From the polymyrcene, a nitrosite of the formula  $C_{40}H_{66}O_{18}N_6$  was formed.

The author has examined the products of the direct oxidation of Para rubber with nitric acid and confirms the observations made by Dittmar (this vol., i, 386). The "dipentene fraction" of rubber oil has been distilled under reduced pressure and the fractions examined as to density and refractive power; the results indicate the presence of a new hydrocarbon.

The results of the investigation tend to confirm Weber's opinion (Abstr., 1900, i, 353) that rubber is a derivative of an aliphatic terpene, that is, it is an unsaturated open-chain hydrocarbon.

J. McC.

**Elemi.** By ALEXANDER TSCHIRCH and J. CREMER (*Arch. Pharm.*, 1902, 240, 293—324).—Forty-six specimens of elemi were examined, some partly crystalline, others amorphous. They were all derived from *Bursaraceae* or *Rutaceae*, and may be referred to three main types, derived from *Canarium*, *Amyris*, and *Protium* respectively. A sample of each of these types was examined chemically.

*Manila elemi*, from *Canarium commune*.—A specimen of soft resin was examined first; it had an acid number 21 and a saponification number 31.5. One per cent. aqueous ammonium and sodium carbonate solutions extract nothing from an ethereal solution of the resin. One per cent. aqueous potassium carbonate solution extracts acids, and  $\alpha$ -maneletic acid,  $C_{37}H_{56}O_4$  (Buri, Abstr., 1878, 439), crystallises from a solution of these in alcohol. This melts at  $215^\circ$ , has a specific rotation  $[\alpha]_D 15.0^\circ$ , acid number 104.5, corresponding with monobasicity, and "saponification" number 197; the last number really indicates the formation of a dipotassium salt, and is not a true saponification number, for mineral acids precipitate the original acid from the alkaline solution. The (mono) *potassium* and *silver* salts were analysed; (mono) *acetyl* and *benzoyl* derivatives were prepared, melting at  $205^\circ$  and  $210^\circ$  respectively; no methoxyl group is present; concentrated nitric acid oxidises the acid, forming a *substance* with the composition  $C_{35}H_{54}O_{20}$ , together with some picric acid. From the mother liquor of the  $\alpha$ -acid, amorphous  $\beta$ -maneletic acid,  $C_{44}H_{80}O_4$ , was isolated; it melts at  $75$ — $76^\circ$ , is optically inactive, and has an acid number 93 corresponding with monobasicity, and a saponification number 115. Manamyrrin,  $C_{30}H_{50}O$  (Vesterberg, Abstr., 1887, 733; 1891, 165), was obtained from the resin, freed from acid, by digesting it with alcohol and crystallising the residue from a mixture of alcohol and ether. This was benzoylated, and the product separated by means of hot 80 per cent. alcohol into a soluble and an insoluble portion melting at  $191$ — $192^\circ$  and  $228$ — $229^\circ$  respectively; by hydrolysis of these,  $\alpha$ - and  $\beta$ -amyrrin were prepared respectively, the latter with more difficulty; they melt at  $181^\circ$  and  $192^\circ$  and have the specific rotations  $91.6^\circ$  and  $99.6^\circ$ . Bryoidin,  $C_{21}H_{42}O_3$ , melting at  $135.5^\circ$ , was prepared by digesting the elemi with dilute alcohol at a gentle heat and evaporating the extract to crystallisation (Flückiger, *Buchner's Rep. Pharm.*, 224); from the mother liquor, a *bitter substance* and sodium chloride were obtained, the latter originating presumably from

melting of the resin, when gathered, with boiling sea-water. By distilling the resin with steam, an *essential oil* was obtained and fractionated; one fraction boiled at  $170-175^{\circ}$  and had sp. gr. 0.955, another boiled at  $175-210^{\circ}$ , and eventually deposited a few crystals melting at  $170^{\circ}$ . *Maneleresen*,  $C_{15}H_{30}O$ , remains after the removal of the other constituents of the resin; it is amorphous and melts at  $63-65^{\circ}$ . In 100 parts of the drug there are contained: manamyryn, 20—25; essential oil, 20—25; bryoidin, 0.8—1;  $\alpha$ -manelemic acid, 5—6;  $\beta$ -manelemic acid, 8—10; maneleresen, 30—35; inorganic constituents and bitter substance, 1—2; impurities, 5—6.

A specimen of hard resin was then examined. It had an acid number 24 and a saponification number 34, and resembled the soft resin, except that it contained more impurities and much less essential oil; the amount of  $\alpha$ -manelemic acid slightly exceeded that of the  $\beta$ -acid.

A third specimen, collected from *Canarium commune*, was examined finally; it contained the same constituents as the other specimens.

*Yucatan elemi*, from *Amyris elemifera*.—The acid number of the specimen examined was 15, the saponification number 33. The constituents were much the same as in the Manila specimens, except that no acids were present. In 100 parts of the drug, there were contained: yucamyryn (melting at  $179^{\circ}$  and containing about equal parts of the  $\alpha$ - and  $\beta$ -modifications), 10—15; essential oil, 8—10; yuceleresen (melting at  $75-77^{\circ}$ ), 60—70; bitter substance and impurities, 4—5. The very large proportion which this resin contains of substances which resist the action of alkalis (resen and amyryn) makes it peculiarly suitable for the basis of a lacquer.

African (Cameroon) elemi, possibly from *Canarium Schweinfurthii*.—The acid number of the specimen examined was 24, the saponification number 38. Only an amorphous *afelemic acid*,  $C_{44}H_{90}O_4$ , was obtained: it melted at  $97-98^{\circ}$  and had an acid number 85, corresponding with monobasicity, and a saponification number 102. *Afamyryn* melted at  $170^{\circ}$  and was not separated into constituents. No bryoidin was found. In 100 parts of the drug there were contained: afamyryn, 20—25; essential oil, 15—20; afelemic acid, 8—10; afeleresen, 40—45.

*Brazilian Protium-Elemi* (*Almessega-Elemi*), from *Almessega brancha*.—A small specimen of this rare elemi was examined; it had an acid number 32 and a saponification number 54.5. The resin contained one-fourth of its weight of impurities; when freed from these, it was found to contain in 100 parts: *protamyryn*,  $C_{30}H_{50}O$  (melting at  $170-171^{\circ}$ ), 30; amorphous *protelemic acid*, 25; *proteleresen*, 37.5. Only traces of essential oil and of bitter substance were present, and bryoidin could not be detected.

It is noteworthy that all the five samples of elemi examined, although they were not derived from the same genus of plants, or even from the same family, yet contained an amyryn—that is, a mixture of two isomeric alcohols with the composition  $C_{30}H_{50}O$ . In the future, Tschirch proposes to regard as elemis proper only those which contain amyryn or an allied substance.

C. F. B.

**Soluble Hydroxyanthraquinone-glucoside contained in Barbadoes Aloes.** By EUGEN AWENG (*Chem. Centr.*, 1902, ii, 368—369; from *Apoth.-Zeit.*, 17, 422).—A large quantity of a double glucoside which resembles that contained in *Frangula* and *Sagrada* (Abstr., 1901, i, 39) has been isolated from the aqueous extract of Barbadoes aloes. This compound gives the reactions of hydroxyanthraquinone and when boiled with hydrochloric acid forms sugar and a substance similar to the  $\psi$ -emodin obtained from *Frangula*. A considerable quantity of  $\psi$ -emodin may also be extracted from the aloes by treating the portion insoluble in water with 95 per cent. alcohol. By the action of bromine or by boiling this  $\psi$ -emodin with alcohol and acid for a long time, emodin and a compound which gives the reactions of rhamnetin are formed. E. W. W.

**Extractum Filicis.** By FRIEDRICH KRAFT (*Chem. Centr.*, 1902, ii, 533—534; from *Schweiz. Woch. Pharm.*, 40, 322—326. Compare Abstr., 1898, i, 40; 1899, i, 32; 1900, i, 49).—Good extracts prepared from the roots of *Aspidium Filix-mas*. contained on the average 3.5 per cent. of filicic acid, 2.5 of flavaspidic acid, 0.05 of albaspidin, 0.1 of aspidinol, 0.1 of flavaspidin, 5 of amorphous acid, and 6 of filicinigrin. Flavaspidic acid may be extracted from crude filicic acid by means of carbon disulphide; it dissolves in 30 parts of hot disulphide, and on cooling 85 per cent. crystallises out. Flavaspidin resembles flavaspidic acid very closely and a small quantity is generally contained in the acid. It is, however, less soluble in carbon disulphide than the acid, crystallises from ethyl acetate in colourless prisms, melts at 199°, and is readily soluble in benzene, chloroform, acetone, or amyl alcohol; it dissolves in alkalis and decomposes carbonates of alkalis or alkaline earths. Filicinigrins consist of decomposition products of the other six components of the extract and form a brown to black, amorphous powder; they are distinguished from the other acids by their insolubility in light petroleum and their physiological inactivity; their solubility is variable and sometimes the powder is infusible.

The chief component of the extract is the amorphous acid, and on this its pharmacological effect depends. It forms a brownish-yellow, amorphous powder, melts at about 60°, is very readily soluble in acetone, chloroform, ethyl acetate, ether, benzene, carbon disulphide, carbon tetrachloride, or glacial acetic acid. The slight reduction effected by boiling the acid with ammoniacal silver solutions or with Fehling's solution is probably due to the presence of decomposition products. Ferric chloride precipitates an amorphous, reddish-brown substance from the alcoholic solution. When melted with alkalis, the acid yields the same products as filicic acid (Boehm) together with methylphloroglucinol methyl ether melting at 118—119° and an acid melting at 137°. The amorphous acid must therefore possess a more complicated structure than filicic acid and may possibly be a homologue containing four butanone rings. E. W. W.

**Reduction of Artemisin by means of Stannous Chloride.** By P. BERTOLO (*Atti R. Accad. Lincei*, 1902, [v], 11, i, 486—492. Compare Abstr., 1901, i, 718).—In order further to study the analogy



in behaviour existing between santonin and artemisin, the author has investigated the reduction of the latter by means of stannous chloride in hydrochloric acid solution. Instead, however, of yielding a compound analogous with santonous acid, this reduction furnishes a product possessing a lactonic structure and having the composition  $C_{15}H_{18}O_3$ , the same as that of santonin. This compound crystallises from alcohol or acetic acid in small, white needles which melt at  $269-270^\circ$  and are slightly soluble in ether, chloroform, benzene, or aqueous alkalis; when suspended in water and treated with ferric chloride or sulphuric acid, it is turned brown, but remains undissolved. On boiling with solutions of the alkalis or alkaline earths, the compound yields salts of a monobasic hydroxy-acid; the *barium*,  $(C_{15}H_{19}O_4)_2Ba$ , *silver*, *lead*, and *copper* salts were prepared; when treated with hydrochloric or sulphuric acid, these salts are slowly converted into the original lactonic compound. The *acetyl* derivative of the latter,  $C_{15}H_{17}O_3Ac$ , crystallises from alcohol, or from a mixture of chloroform or benzene with light petroleum, in white, shining leaflets or needles which melt at  $205-206^\circ$ ; on boiling with potassium hydroxide solution and acidifying with hydrochloric acid the original lactone is re-formed.

These results show that, in place of the carbonyl group present in artemisin, the reduction product of the latter contains a hydroxyl group of a phenolic nature. When fused with alkali, the compound yields 1:4-dimethyl- $\beta$ -naphthol; this compound is not obtained either from santonin or artemisin and the author concludes that the ketonic groups in the molecules of these two substances occupy corresponding positions.

On reducing artemisin by means of zinc dust and acetic acid, a dextrorotatory compound of a lactonic nature melting at  $275^\circ$  is obtained.

When artemisin is treated with sodium carbonate and the solution acidified with dilute sulphuric acid, a compound is obtained crystallising from water in long, silky needles which melt at  $121-122^\circ$  and in alcoholic solution are dextrorotatory.

T. H. P

**Degradation of Brazilin.** By WILLIAM H. PERKIN, jun. (*Ber.*, 1902, 35, 2946—2947).—A claim of priority (see *Proc.*, 1902, 18, 147) over Kostanecki and Paul (this vol., i, 686).

R. H. P.

**Dyeing of Animal Fibres by Acid Colouring Matters.** By PAUL SISLEY (*Bull. Soc. Chim.*, 1902, [iii], 27, 901—914).—The author determines the partition coefficient of picric acid between water and toluene, water and ether, and water and amyl alcohol, and shows that in all these cases the partition coefficient depends on the concentration. Similar results were obtained with various acid colouring matters. Experiments were also carried out on the extraction of picric acid both in neutral and in acid solution by silk, amyl alcohol, and toluene, when it was found that the amount of picric acid extracted was much greater in acid solution than in neutral. This the author explains by the diminution of the dissociation of picric acid by the acid added.

[No reference is made to the work of Walker and Appleyard (Trans., 1896, 69, 1334) on this subject.] A. F.

**Composition of the Tanning Material 'Taran.'** By F. SAROSEK (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 504).—Taran is a root used for tanning in the native tanneries of Central Asia; it contains 17 per cent. of tannin which is taken up by leather; ellagic acid is also present. T. H. P.

**Action of Hydroxylamine on Ethyl Dimethylpyronedicarboxylate.** By CARLO PALAZZO (*Atti R. Accad. Lincei*, 1902, [v], 11, i, 562—565).—The action of hydroxylamine on the ethyl dimethylpyronedicarboxylate prepared by Conrad and Guthzeit (Abstr., 1886, 333) in presence of sodium carbonate yields a compound which has probably the constitution  $\text{CMe} \begin{smallmatrix} \text{N.OH} \\ \diagdown \\ \text{C.CO}_2\text{Et} \end{smallmatrix}$  and separates from water in shining, white needles containing water of crystallisation; it is soluble in acetone, hydrochloric acid, or acetic acid, and in acetic acid solution gives the normal depression of freezing point. The anhydrous compound melts at 164° and immediately afterwards undergoes vigorous decomposition. It decolorises permanganate in the cold and in acetic acid solution absorbs bromine, whilst when heated with hydriodic acid, it evolves ethyl iodide. With silver nitrate, it gives a white precipitate, which has the composition  $\text{C}_6\text{H}_5\text{O}_3\text{NAg}, 2\text{H}_2\text{O}$ , and is rapidly turned violet by the action of direct sunlight. T. H. P.

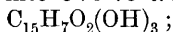
**Chromone.** By R. HEYWANG and STANISLAUS VON KOSTANECKI (*Ber.*, 1902, 35, 2887—2891. Compare Abstr., 1901, i, 735; and this vol., i, 303, 690).—Chromone derivatives have been prepared (*loc. cit.*) by condensing derivatives of *o*-hydroxyacetophenone and ethyl oxalate. Ruhemann and Stapleton (Trans., 1900, 77, 1179) prepared chromone itself from phenoxyfumaric acid. Chromone-2-carboxylic acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \\ \text{C.CO}_2\text{H} \\ \diagdown \\ \text{CO.CH} \end{smallmatrix}$ , has now been prepared from *o*-hydroxyacetophenone, ethyl oxalate, and sodium; the ethyl *o*-hydroxybenzoylpyruvate first formed was not purified, but converted into chromone-2-carboxylic acid by treatment with hydrogen chloride in alcoholic solution; the acid crystallised in needles decomposing at 252° (compare Ruhemann and Stapleton) with evolution of carbon dioxide and formation of chromone. Chromone is decomposed by boiling with alcoholic sodium ethoxide into *o*-hydroxyacetophenone and formic acid. The melting point of  $\alpha$ -naphthachromone (this vol., i, 303), which has not been previously recorded, is 125°.

The paper contains a list of the chromone derivatives which up to the present time have been prepared. K. J. P. O.

**3:3':5'-Trihydroxyflavone.** By STANISLAUS VON KOSTANECKI and PETER WEINSTOCK (*Ber.*, 1902, 35, 2885—2887).—2:4-Diethoxy-3':5'-dimethoxybenzoylacetophenone,  $\text{C}_6\text{H}_3(\text{OEt})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_3(\text{OMe})_2$ , is prepared by heating 2:4-diethoxyacetophenone and ethyl 3:5-di-

methoxybenzoate with sodium at  $130^{\circ}$ , it crystallises in needles melting at  $139.5^{\circ}$ , and gives a dirty red coloration with ferric chloride. When the  $\beta$ -diketone is boiled with hydriodic acid, it is converted into trihydroxyflavone, which, for purposes of purification, is methylated by means of methyl sulphate and potassium hydroxide.

3:3':5'-Trimethoxyflavone,  $\text{OMe} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{C} \cdot \text{C}_6\text{H}_3(\text{OMe})_2 \\ \text{CO} \cdot \text{CH} \end{smallmatrix}$ , crystallises in needles melting at  $181-182^{\circ}$ , and by prolonged boiling with hydriodic acid is converted into 3:3':5'-trihydroxyflavone,



the latter forms crusts of microscopic needles melting at  $329^{\circ}$ , dissolves in sodium hydroxide with a greenish-yellow coloration, and in concentrated sulphuric acid with a yellow coloration and a greenish fluorescence. 3:3':5'-Triacetoxylavone,  $\text{C}_{15}\text{H}_7\text{O}_2(\text{OAc})_3$ , crystallises in white needles melting at  $187^{\circ}$ .  
K. J. P. O.

**Hyoscyne and Atroscine.** By OSWALD HESSE (*J. pr. Chem.*, 1902, [ii], 66, 194—205. Compare this vol., i, 51).—Freshly prepared hyoscyne hydrobromide has  $[\alpha]_D - 27.7^{\circ}$  at  $15^{\circ}$ ; after four weeks, the rotation has diminished to  $[\alpha]_D - 25.9^{\circ}$ . This is probably due to the existence of a labile modification of hyoscyne.

Atroscine occurs in a crystalline and an amorphous form. The latter is obtained on separation of the alkaloid from its salts, or from the crystalline form when placed over concentrated sulphuric acid or phosphoric acid. Atroscine monohydrate and dihydrate crystallise together on addition of a crystal of each to the syrupy atroscine at  $5-8^{\circ}$ . At  $0^{\circ}$  the dihydrate, at  $15-20^{\circ}$  the monohydrate, is formed. In presence of a trace of the monohydrate at  $20^{\circ}$ , the dihydrate changes slowly to the monohydrate; the change takes place more quickly in contact with ether at  $15^{\circ}$ . When pure, the dihydrate is not less stable than the monohydrate (compare Gadamer, this vol., i, 173; Kunz-Krause, this vol., i, 174).

When molecular proportions of tropine platinichloride and oscine platinichloride (m. p.  $210-212^{\circ}$ ) are dissolved together in hot water, dark orange-red crystals,  $(\text{C}_8\text{H}_{15}\text{ON}, \text{C}_8\text{H}_{13}\text{O}_2\text{N})_2, \text{H}_2\text{PtCl}_6$ , separate which contain no water of crystallisation, melt and decompose at  $202-204^{\circ}$ , and are probably identical with Ladenburg's  $\psi$ -tropine platinichloride (this vol., i, 390). The remainder of the paper is a reply to E. Schmidt's note to Gadamer's paper.  
G. Y.

**$\beta$ -Methylmorphimethine.** By LUDWIG KNORR and SAMUEL SMILES (*Ber.*, 1902, 35, 3009—3010. Compare *Abstr.*, 1894, i, 430).— $\beta$ -Methylmorphimethine is formed when the  $\alpha$ -compound is boiled with acetic anhydride, water, or 50 per cent. alcohol, but not with absolute alcohol. It is best prepared by boiling the  $\alpha$ -compound with 60 per cent. alcohol containing 10 per cent. of potassium hydroxide, and crystallises in prisms melting at  $134-135^{\circ}$ ;  $[\alpha]_D + 438^{\circ}$  ( $c=1$ ) in solution in 97 per cent. alcohol. The base forms a violet solution in sulphuric acid, which becomes blue and then green when ice-water is added. The *methiodide* melts at about  $300^{\circ}$  and has  $[\alpha]_D + 233^{\circ}$  ( $c=0.6$ ) in solution in 97 per cent. alcohol. The *benzoate* crystallises in small

needles melting at  $157^{\circ}$  and has  $[\alpha]_D + 254^{\circ}$  ( $c=1$ ) in aqueous solution. The oily base, as obtained by the action of acetic anhydride on the  $\alpha$ -compound, can be readily purified by means of the benzoate.

A. H.

**A Fourth Methylmorphimethine.** By LUDWIG KNORR and JOHN HAWTHORNE (*Ber.*, 1902, 35, 3010—3013. Compare the preceding abstract).— $\gamma$ -Methylmorphimethine (Schryver and Lees, *Trans.*, 1901, 79, 563) is converted by boiling alcoholic potash into  $\delta$ -methylmorphimethine, which crystallises in prisms melting at  $111$ — $113^{\circ}$  and has  $[\alpha]_D + 256.6^{\circ}$  ( $c=1.243$ ) in solution in methyl alcohol. The base is as a rule more readily soluble than the  $\gamma$ -isomeride. The methiodide of  $\delta$ -methylmorphimethine crystallises in rectangular plates which melt and decompose at about  $282$ — $284^{\circ}$ ;  $[\alpha]_D + 150.7^{\circ}$  ( $c=1.003$ ) in absolute alcohol. This substance can also be obtained by heating the methiodide of the  $\gamma$ -base with dilute aqueous potash. The benzoate crystallises in slender needles, melts indefinitely at  $99$ — $108^{\circ}$ , and has  $[\alpha]_D + 181.1^{\circ}$  ( $c=0.6315$ ) in solution in 99 per cent. alcohol.  $\gamma$ -Methylmorphimethine benzoate also melts indefinitely at about  $100^{\circ}$ , is more readily soluble in water than the  $\gamma$ -derivative, and has  $[\alpha]_D + 41.3^{\circ}$  ( $c=0.8685$ ) in solution in 99 per cent. alcohol.

A. H.

**Morphigenine and Epiosine.** By ERNST VAHLEN (*Ber.*, 1902, 35, 3044—3047. Compare *Arch. Path. Pharm.*, 48, 368).—In reply to the criticism of Pschorr (this vol., i, 672), the author maintains that the physiological action of epiosine resembles that of morphine and is not due to the formation of methæmoglobin in the blood of the animals experimented on.

A. H.

**Addition of Sulphurous Acid on Quinidine.** By WILHELM KÖNIGS and HANS SCHÖNEWALD (*Ber.*, 1902, 35, 2980—2991).—An aqueous solution of quinidine, which has been saturated with sulphur dioxide, deposits, after some weeks, the monobasic acid,  $C_{20}H_{26}O_7N_2S_2$ ; this crystallises with  $4H_2O$  and decomposes at about  $260^{\circ}$ . Its solutions in dilute sulphuric acid exhibit a blue fluorescence and give the colorations with chlorine water and ammonia characteristic of quinine and quinidine. The hydrobromide and hydrochloride are both crystalline salts. The ammonium salt, with  $4H_2O$ , is amorphous, and has  $[\alpha]_D 160.42'$  at  $19.5^{\circ}$ . The barium and silver salts were obtained as yellow, amorphous precipitates, and the monobromo-derivative,  $C_{20}H_{25}O_7N_2BrS_2$ , as a pale yellow, crystalline precipitate. When oxidised with chromic acid, the acid yields quininic acid, and when oxidised with permanganate in the cold, the sulphonic acid,  $C_{20}H_{28}O_8N_2S_2$ , which crystallises with  $4H_2O$  in beautiful, white, six-sided leaflets and forms a pale yellow, amorphous, hygroscopic ammonium salt.

Quinine yields the analogous additive product,  $C_{20}H_{26}O_7N_2S_2 \cdot H_2O$ , only in small quantities.

R. H. P.

**Pipecoline Derivatives.** By G. VON OSTOJA BALICKI (*Ber.*, 1902, 35, 2780—2782).—Nitrosopipecoline is an oil boiling at  $123^{\circ}$  under

31 mm. pressure; it is prepared by treating a solution of pipercoline in cold dilute sulphuric acid with sodium nitrite. On reduction with zinc dust and water, the nitrosoamine yields *pipecolylhydrazine* (1-*amino-pipercoline*); this product is a colourless oil boiling at 156–160° which has a sp. gr. 0.90058 at 19°/4°. The *s*-hydrazine solidifies, on cooling, in solid carbon dioxide and yields uncrystallisable salts with halogen hydracids; the *picrate* crystallises from alcohol in orange-yellow needles and melts at 143°.

A crystalline *hydrazone*,  $C_6H_{12}N \cdot N : CH \cdot C_6H_4 \cdot NO_2$ , melting at 63°, was obtained from the hydrazine and *m*-nitrobenzaldehyde, but benzaldehyde, piperonaldehyde, acetone, and acetophenone yield oily hydrazones, and dextrose furnishes only an uncrystallisable osazone.

G. T. M.

**Condensation of Aldehydes with Ethyl Cyanoacetate.** I. By ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1901–1902, 37, 593–611. Compare Abstr., 1900, i, 52 and 111).—The author has shown (*loc. cit.*) that the reaction between an aldehyde, ethyl cyanoacetate, and ammonia leads, not to a piperidine derivative, as was to be expected, but to a pyridine compound, there being an apparent disappearance of hydrogen. The latter the author has now traced, and he finds that it is used up in converting some of the cyanoacetamide derivative, which is an intermediate product in the above reaction, into the corresponding saturated compound. These reactions are expressed by the equations: (1)  $R \cdot CHO + CN \cdot CH_2 \cdot CO_2Et + NH_3 = Et \cdot OH + H_2O + R \cdot CH : C(CN) \cdot CO \cdot NH_2$ . (2)  $R \cdot CH : C(CN) \cdot CO \cdot NH_2 + H_2 = R \cdot CH_2 \cdot CH(CN) \cdot CO \cdot NH_2$ . This reaction may also be employed to obtain, not only dicyanodioxypyridines, but also monoalkylcyanoacetamides. The reactions of certain other aldehydes with ammonia and ethyl cyanoacetate have been studied, the results being as follows:

*m*-Tolualdehyde, ammonia, and ethyl cyanoacetate give rise to three products: (1) The *ammonium* derivative of *m*-tolyl*dicyanoglutaconimide*,  $C_6H_4Me \cdot C \begin{smallmatrix} \diagup C(CN) \diagdown \\ \diagdown CH(CN) \diagup \end{smallmatrix} \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{smallmatrix} N \cdot NH_4$ , the main product of the reaction, crystallises from water in colourless, anhydrous needles which are soluble in pyridine and do not melt even at 290°; when heated with 60 per cent. sulphuric acid, it yields *m*-tolyl- $\gamma$ -cyanovinylacetic acid,  $C_6H_4Me \cdot C : (CH \cdot CN) \cdot CH_2 \cdot CO_2H$ , to be described in a later communication; the *silver* and *copper* (+ 6H<sub>2</sub>O) salts were prepared. (2) *m*-Tolylcyanoacetamide,  $C_6H_4Me \cdot CH_2 \cdot CH(CN) \cdot CO \cdot NH_2$ , crystallises from water in broad, nacreous laminae which melt at 108.5–109.5°, and are soluble in alcohol, ether, or pyridine. (3) A compound almost insoluble in water and melting, in the crude condition, at 194–198°.

Cuminaldehyde, ammonia, and ethyl cyanoacetate yield two products: (1) The *ammonium* derivative of *propylphenyl- $\beta\beta$ -dicyanoglutaconimide*,  $C_6H_4Pr \cdot C \begin{smallmatrix} \diagup C(CN) \diagdown \\ \diagdown CH(CN) \diagup \end{smallmatrix} \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{smallmatrix} N \cdot NH_4$ , crystallising from water in yellowish, slender needles, dissolving in alcohol or pyridine, and remaining unfused at 290°; when heated with 60 per cent. sulphuric acid, it yields  $\beta$ -propylphenyl- $\gamma$ -cyanovinylacetic (cumyl- $\gamma$ -cyanovinylacetic acid), to be described in another communication. The *copper*

(+8H<sub>2</sub>O) and *silver* salts were prepared and analysed. The *coniine* derivative, C<sub>16</sub>H<sub>18</sub>O<sub>2</sub>N<sub>3</sub>·C<sub>8</sub>H<sub>17</sub>N, is precipitated either in prisms or needles melting at 251—252°; the *nicotine* salt forms a minutely crystalline precipitate melting at about 300°. (2) *Cumylcyanoacetamide* ( $\alpha$ -cyanopropylphenylhydrocinnamamide),

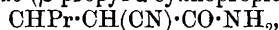


separates from water in long, colourless, silky needles which are soluble in alcohol or pyridine and melt at 144—145°; it sublimes, but with partial decomposition. Its solution is neutral and develops ammonia when heated with potassium hydroxide.

*n*-Butaldehyde, ammonia, and methyl (or ethyl) cyanoacetate interact with the formation of: (1) The *ammonium* derivative of *propyldicyanoglutaconimide*, CH<sub>2</sub>Et·C $\begin{smallmatrix} \text{C}(\text{CN})-\text{CO} \\ \text{CH}(\text{CN})\cdot\text{CO} \end{smallmatrix}$ ·N·NH<sub>4</sub>, which separates

from water in slender, silky needles soluble in pyridine; it has a bitter taste, recalling those of quinine and magnesium sulphate. When heated with 60 per cent. sulphuric acid, it yields  $\beta$ -propyl- $\gamma$ -cyano-vinylacetic acid, to be described later; the silver salt was prepared.

(2) *Butylcyanoacetamide* ( $\beta$ -propyl- $\alpha$ -cyanopropionamide),



which crystallises from water in thin, nacreous laminae melting at 125.5—126.5° and subliming in iridescent plates; it gives a neutral aqueous solution, is soluble in pyridine, and yields ammonia when heated with potassium hydroxide solution.

Benzaldehyde, ammonia, and ethyl cyanoacetate yield (1) benzylcyanoacetamide, (2) phenyldicyanodioxypyridine (*loc. cit.*), and (3) a compound, insoluble in water and probably identical with that of Carrick.

Anisaldehyde, ammonia, and ethyl cyanoacetate yield *anisylcyanoacetamide*, OMe·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CH(CN)·CO·NH<sub>2</sub>, which crystallises from ether in slender, silky needles soluble in water or alcohol and melting at 172°.

From heptaldehyde, ammonia, and ethyl cyanoacetate are obtained the two products: (1) the ammonium derivative of  $\gamma$ -hexyl- $\beta\beta$ -dicyanodioxypyridine, and (2) heptyl- $\alpha$ -cyanoacetamide, which will be described in a later communication.

T. H. P.

**Action of Sulphuryl Chloride on Pyrrole.** By GIROLAMO MAZZARA (*Gazzetta*, 1902, 32, i, 510—514).—The interaction of 1 mol. of sulphuryl chloride and 1 mol. of pyrrole yields an unstable *monochloro*-derivative of the latter, which is a heavy, yellow liquid and decomposes explosively, whilst with 2 mols. of the chloride a *dichloro*-compound is obtained which, when repeatedly distilled in a current of steam, is converted first into a white, buttery mass and afterwards into carbonaceous matter. Both these compounds are volatile in a current of steam and colour sulphuric acid green, whilst pine shavings moistened with hydrochloric acid are turned red by them.

Tetrachloropyrrole, C<sub>4</sub>NHCl<sub>4</sub>, is obtained in good yield by the interaction at 0° of an absolute alcoholic solution of pyrrole with sulphuryl chloride (4 mols.), and is identical with Ciamician and Silber's (Abstr., 1885, 1077) compound.

T. H. P.

**Formation of Pyrrole Derivatives from *iso*Nitrosoketones.** By LUDWIG KNORR and H. LANGE (*Ber.*, 1902, 35, 2998—3008. Compare *Annalen*, 1886, 236, 296).—Pyrrole derivatives have hitherto been obtained from three different *isonitroso*-derivatives by reduction in presence of a ketone or ketonic ester, and the reaction has now been extended to four additional *isonitroso*-compounds. The intermediate formation of amino-ketones is rendered probable by the fact that in many cases the substitution of aminoacetophenone for *isonitroso*acetophenone was accompanied by a considerable increase in the yield, whilst in certain cases pyrrole derivatives were obtained from the amino-ketone but not from the *isonitroso*-ketone. In the new series of syntheses, the following results were obtained. *iso*Nitrosoacetophenone yields pyrrole derivatives with ethyl acetoacetate (the yield being 56 per cent.), acetylacetone (40 per cent.), ethyl acetonedicarboxylate (3 per cent.), benzoylacetone (4.5 per cent.), but does not yield them with ethyl oxalacetate, ethyl acetoneoxalate, dibenzoylmethane, formylacetone, phenylacetone, diphenylacetone, or acetophenone. Aminoacetophenone gives pyrrole derivatives with ethyl acetoacetate (almost 100 per cent.), acetylacetone (100 per cent.), ethyl acetonedicarboxylate (9 per cent.), benzoylacetone (38 per cent.), and in traces with ethyl acetoneoxalate, formylacetone, and phenylacetone, whilst it does not yield them with ethyl oxalacetate, dibenzoylmethane, benzoylaldehyde, diphenylacetone, and deoxybenzoin.

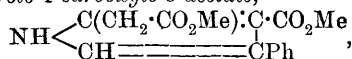
*iso*Nitrosodeoxybenzoin yields pyrrole derivatives with ethyl acetoacetate (25 per cent.) and with acetylacetone (50 per cent.), but not with deoxybenzoin.

*iso*Nitrosoacetone yields pyrrole derivatives with ethyl acetoacetate (50 per cent.), acetylacetone (33 per cent.), and in traces with benzoylacetone. Finally, dimethyl *isonitroso*acetonedicarboxylate yields a pyrrole derivative with dimethyl acetonedicarboxylate.

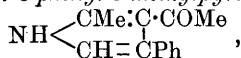
Acetone and methyl ethyl ketone with *isonitroso*acetone, and acetone with *isonitroso*acetophenone give products which only yield the reactions of pyrrole derivatives after treatment with strong sulphuric acid. These cases seem to indicate that the reaction proceeds in two stages.

The following new compounds have been obtained by this method.

*Ethyl 3-phenyl-5-methylpyrrole-4-carboxylate*,  $\text{NH} \begin{array}{c} \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \\ | \\ \text{CH} = \text{CPh} \end{array}$ , is prepared from ethyl acetoacetate and *isonitroso*acetophenone or aminoacetophenone, melts at 105°, and gradually becomes yellow in the air. The corresponding *acid* melts and loses carbon dioxide at 115°. *Dimethyl 3-phenylpyrrole-4-carboxylo-5-acetate*,



prepared from methyl acetonedicarboxylate and *isonitroso*acetophenone, melts at 126°. *4-Acetyl-3-phenyl-5-methylpyrrole*,



prepared from *isonitroso*acetophenone and acetylacetone, melts at 151°, and is converted by the action of benzaldehyde and aqueous potash into *4-cinnamoyl-3-phenyl-5-methylpyrrole* melting at 167°.

4-Benzoyl-3-phenyl-5-methylpyrrole,  $\text{NH} \begin{smallmatrix} \text{CMe}:\text{CBz} \\ \text{CH}=\text{CPh} \end{smallmatrix}$ , prepared from isonitrosoacetophenone and benzoylacetone, melts at  $231^\circ$ . Ethyl 2:3-diphenyl-5-methylpyrrolecarboxylate,  $\text{NH} \begin{smallmatrix} \text{CMe}:\text{C}\cdot\text{CO}_2\text{Et} \\ \text{CPh}=\text{CPh} \end{smallmatrix}$ , prepared from ethyl acetoacetate and isonitrosodeoxybenzoin, is a colourless, crystalline substance.

4-Acetyl-2:3-diphenyl-5-methylpyrrole,  $\text{NH} \begin{smallmatrix} \text{CMe}:\text{CAc} \\ \text{CPh}:\text{CPh} \end{smallmatrix}$ , is prepared from acetylacetone and isonitrosodeoxybenzoin, and is converted by benzaldehyde into 4-cinnamoyl-2:3-diphenyl-5-methylpyrrole, which melts at  $215^\circ$ .

The reaction product obtained from acetone and isonitrosoacetone does not contain a pyrrole derivative, but one is formed when it is mixed with sulphuric acid. The expected dimethylpyrrole could not be obtained pure, a large proportion of dimethylpyrazine being simultaneously formed. A. H.

[Double Salts of Thallium and Alkaloids with Hydracids.] By CARL RENZ (*Ber.*, 1902, 35, 2768—2774. Compare R. J. Meyer, *Abstr.*, 1900, ii, 655, and this vol., i, 393).—*Thallic bromide pyridine hydrobromide*,  $(\text{TlBr}_3)_2(\text{C}_5\text{NH}_5, \text{HBr})_3$ , obtained by dissolving the corresponding double chloride in hot concentrated potassium bromide solution, crystallises on cooling in pale yellow needles melting at  $174^\circ$ .

*Thallic chloride piperidine hydrochloride*,  $\text{TlCl}_3(\text{C}_5\text{NH}_{11}, \text{HCl})_3$ , unlike the other organic double salts of the type, is extremely soluble and separates from a concentrated solution of its generators only after further evaporation under reduced pressure; it forms long, prismatic crystals, soluble in alcohol but not in ether.

*Thallic iodide hyoscyamine hydriodide*,  $\text{TlI}_3\cdot\text{C}_{17}\text{H}_{23}\text{O}_3\text{N}, \text{HI}$ , separates in red crystals from a concentrated solution of potassium iodide and the corresponding double chloride and melts at  $200^\circ$ .

*Thallic iodide atropine hydriodide*,  $\text{TlI}_3\cdot\text{C}_{17}\text{H}_{23}\text{O}_3\text{N}, \text{HI}$ , resembles the preceding compound and melts at  $192^\circ$ .

*Thallic chloride cocaine hydrochloride*,  $\text{TlCl}_3(\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}, \text{HCl})_2$ , resulting from the interaction of its generators in concentrated solutions, crystallises in white needles.

*Thallic chloride strychnine hydrochloride*,  $\text{TlCl}_3(\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2, \text{HCl})_2$ , obtained like the preceding double salt, crystallises from a mixture of alcohol and dilute hydrochloric acid in iridescent leaflets decomposing at  $240^\circ$ .

*Thallic chloride cinchonine hydrochloride*,  $\text{TlCl}_3(\text{C}_{19}\text{H}_{22}\text{ON}_2, \text{HCl})_2\cdot 4\text{H}_2\text{O}$ , crystallises from hot dilute hydrochloric acid in aggregates of silky needles.

*Thallic chloride quinine hydrochloride*,  $\text{TlCl}_3\cdot\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2, \text{HCl}, 2\text{H}_2\text{O}$ , closely resembles the preceding compound.

Thallic chloride yields less stable double salts with coniine, nicotine, and 2:6-lutidine; with morphine, it gives rise to an insoluble yellowish-white powder,  $(\text{TlCl}_3)_6\cdot\text{C}_{17}\text{H}_{19}\text{O}_2\text{N}$ .



Dimethylaniline interacts with thallic chloride, giving rise to a violet colouring matter resembling crystal-violet; dimethyl-*o*-toluidine furnishes a similar dye of redder shade.

Methyldiphenylamine, when left in contact with an alcoholic solution of thallic chloride, becomes oxidised to a blue colouring matter which is probably identical with diphenylamine-blue. G. T. M.

**The Three Isomeric Cyanides of Pyridine.** By RUDOLF CAMPS (*Arch. Pharm.*, 1902, 240, 366—370).—All three cyanopyridines can be obtained by distilling under diminished pressure a mixture of phosphoric oxide with the amide of the corresponding pyridine-carboxylic acids (this vol., i, 824). In the case of the 4-compound, it was found also that the cyanide can be obtained by distilling a mixture of the acid with lead thiocyanate.

2-Cyanopyridine is not reduced to pyridylmethylaniline by 3 per cent. sodium amalgam; pyridine and hydrocyanic acid are formed, and at the same time a certain amount of hydrolysis to the amide and the acid takes place. Nor can 4-cyanopyridine be reduced with aluminium amalgam; the acid is formed.

*Cyanopyridines (pyridyl cyanides)*,  $C_5NH_4 \cdot CN$ .—The 2-compound (*picolinonitrile*) melts at 29°. The 4-isomeride (*isonicotinonitrile*) melts at 79°; its *hydrochloride*, *platinichloride*, and *aurichloride* melt and decompose at 199°, 293°, and 185° respectively; the *mercurichloride*,  $C_5NH_4 \cdot CN, HgCl_2$ , was analysed. C. F. B.

**Ethyl 2:6-Dimethyl-4-chloronicotinate.** By AUGUST MICHAELIS and R. HANISH (*Ber.*, 1902, 35, 3156—3161).—The compound previously described as 2:6-dimethylchloroethoxylutidine (*Abstr.*, 1901, i, 609) is now shown to be ethyl 2:6-dimethyl-4-chloronicotinate (compare Collie, *Trans.*, 1891, 59, 176).

The *aurichloride* of the ester melts at 116—117° and the *picrate* at 129°. Methyl iodide at 95—100° transforms the ester into *ethyl 2:6-dimethyl-4-iodonicotinate methiodide*,  $C_{10}H_{12}O_2NI, MeI$ , melting at 194°. Methyl bromide yields the *methobromide*,  $C_{10}H_{12}O_2NCl, MeBr$ , melting at 198°. Concentrated hydrochloric acid at 150° converts the ester into  $\gamma$ -lutidone melting at 224—225°. Aniline yields Conrad and Epstein's phenylaminolutidine (*Abstr.*, 1887, 501). 4-Chloro-2:6-dimethylnicotinic acid melts at 168—170°, and when heated at 175° loses carbon dioxide and yields chlorolutidine. 4-Ethoxy-2:6-dimethylnicotinic acid crystallises from hot water in colourless needles containing 3H<sub>2</sub>O; when anhydrous, it melts at 200—201°. The *sodium salt*, *silver salt*, and the *hydrochloride* melting at 127° have been prepared.

J. J. S.

**Derivatives of 2:6-Dichloroisonicotinic Acid.** By KARL BITTNER (*Ber.*, 1902, 35, 2933—2936).—2:6-*Dianilinopyridine-4-carboxyanilide*,  $C_5NH_2(NHPh)_2 \cdot CO \cdot NHPh$ , prepared by heating dichloroisonicotinic acid with aniline, crystallises from alcohol in olive-green, glistening, hexagonal plates and melts at 140—141°. The *acid*,  $C_5NH_2(NHPh)_2 \cdot CO_2H$ , crystallises from alcohol in yellow, micro-

scopic needles and does not melt at 300°. The *methyl* ester,  $C_5NH_2(NHPh)_2 \cdot CO_2Me$ , crystallises from alcohol and melts at 142°.

2:6-Dithiopyridine-4-carboxylic acid,  $C_5NH_2(SH)_2 \cdot CO_2H$ , forms small, reddish-yellow needles and melts at 230°. The *potassium* salt,  $KS \cdot C_5NH_2(SH)_2 \cdot CO_2K, EtOH$ , separates from alcohol in insoluble, glistening, golden flakes and does not lose its alcohol of crystallisation by long drying at 110°. The *methyl* ester,  $C_5NH_2(SH)_2 \cdot CO_2Me$ , separates from dilute methyl alcohol in microscopic, cinnabar-red needles, melts at 156°, and has a characteristic odour. The acid appears to be oxidised by nitric acid to the corresponding disulphonic acid.  
T. M. L.

**Some Carbamides, Thiocarbamides, and Ethyl Carbamates of Pyridine.** By RUDOLF CAMPS (*Arch. Pharm.*, 1902, 240, 345—365).—*iso*Nicotinic acid was found to melt at 315°.

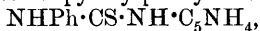
The carboxylic acids,  $C_5NH_4 \cdot CO_2H$ , were converted into the esters  $C_5NH_4 \cdot CO_2Et$  by heating them on the water-bath with a mixture of equal weights of alcohol and sulphuric acid; the 4-*ester*, boiling at 218°, takes up ethyl iodide, and when the additive compound is treated with moist silver oxide it forms a silver salt from which, by treatment with hydrogen sulphide and evaporation of the filtered liquid,

the *ethylbetaine* of *isonicotinic* acid,  $C \begin{array}{c} \diagup CH \cdot CH \diagdown \\ \diagdown CO - O \diagup \\ \diagup CH \cdot CH \diagdown \end{array} NEt$ , melting and de-

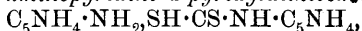
composing at 241°, was obtained. The esters were converted into the amides  $C_5NH_4 \cdot CO \cdot NH_2$  by pouring concentrated ammonia over them and allowing the mixture to remain at the ordinary temperature; the 4-*amide* melts at 155° when anhydrous, at 117—120° when crystallised with water. The amides were converted into the aminopyridines,  $C_5NH_4 \cdot NH_2$ , by treatment with a solution of bromine in aqueous potassium hydroxide; at the same time, *dibromocaminopyridines*,  $C_5NH_2Br_2 \cdot NH_2$ , melting at 137°, 148°, and 167° in the case of the 2-, 3-, and 4-compounds respectively, were formed in small amount, and also some *bromo-2-aminopyridine*,  $C_5NH_5Br \cdot NH_2$ , melting at 106—107° and crystallising in slender, lustrous needles, and a *substance* melting at 126°, probably a complex carbamide derivative (compare Pollak, *Abstr.*, 1895, i, 391), in the cases of the 2- and 3-compounds respectively. The amines condense with acetic anhydride to form the *acetylaminopyridines*,  $C_5NH_4 \cdot NHAc$ , or “*antifebrines*” of the pyridine series, which melt respectively at 71°, 133°, and 150° (when anhydrous; the last at 124° when crystallised with water). The amines are all converted into hydroxypyridines (pyridones) when diazotised in cold sulphuric acid solution (compare Marckwald, *Abstr.*, 1894, i, 381, who obtained chloropyridine only when diazotising in hydrochloric acid solution).

With ethyl chloroformate in ethereal solution, they form *ethyl pyridinecarbamates* (*urethanes*),  $CO_2Et \cdot NH \cdot C_5NH_4$ , melting respectively at 105°, 90°, and 129°, and sometimes also a little of the *di-pyridylcarbamides*,  $CO(NH \cdot C_5NH_4)_2$ , which can always be obtained by

the further action of the amine on the carbamate, and melt at 175°, 225°, and 208° respectively; with aniline, the 2-carbamate forms 2-pyridylphenylcarbamide,  $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_5\text{NH}_4$ , crystallising in slender needles and melting at 180°. With phenylthiocarbimide, the aminopyridines condense to pyridylphenylthiocarbamides,



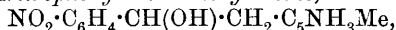
which melt at 171°, 164°, and 148° respectively. When heated with carbon disulphide in alcoholic solution, 2-aminopyridine forms di-pyridylthiocarbamide,  $\text{CS}(\text{NH}\cdot\text{C}_5\text{NH}_4)_2$ , crystallising in lustrous, highly refractive, long needles or prisms, and melting at 163°, along with small quantities of substances melting at 147° and 85° respectively; the 4-amine forms ethyl 4-pyridylthiocarbamate,  $\text{OEt}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_5\text{NH}_4$ , crystallising in needles and melting at 110° when anhydrous, at 92–93° when crystallised with water, together with a yellow substance, probably 4-aminopyridine 4-pyridyldithiocarbamate,



which melts and decomposes at 152°.

C. F. B.

**Condensation of 2:4-Lutidine with *p*-Nitrobenzaldehyde.** By R. KNICK (*Ber.*, 1902, 35, 2790–2793. Compare Bialon, this vol., i, 828).—*p*-Nitrophenyl-2:4-lutidylalkine,



produced by heating 2:4-lutidine and *p*-nitrobenzaldehyde at 130–135°, crystallises from alcohol in yellow plates melting at 168–169°; the base is insoluble in water and dissolves only sparingly in the other organic solvents. The hydrochloride separates in fern-like crystals and melts at 242°; the picrate crystallises from water in golden spangles containing  $1\text{H}_2\text{O}$ , the anhydrous salt melts at 171°; the benzoate,  $\text{C}_{21}\text{H}_{18}\text{O}_4\text{N}_3$ , forms white flakes decomposing at 214°; the platinichloride melts at 219°.

The preceding base yields *p*-aminophenyl-2:4-lutidylalkine on reduction with tin and hydrochloric acid; this melts at 130° and yields a platinichloride crystallising in orange-red needles and decomposing at 222°; the mercurichloride separates in needles and melts at 236°.

*p*-Nitro-4-methylstilbazole,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{C}_5\text{NH}_3\text{Me}$ , is a by-product in the preceding condensation; it crystallises in pale yellow, lustrous leaflets and melts at 134°; the hydrochloride separates in yellow needles melting at 234–235°; the platinichloride and mercurichloride melt respectively at 237° and 187° respectively; the base also yields a dibromide.

*p*-Amino-4-methylstilbazole, produced by reducing the preceding base, melts at 119° and yields a hydrochloride and a dibromide, separating in white crystals and decomposing respectively at 208° and 157°; the platinichloride and mercurichloride form yellow needles; the former darkens at 280° without melting, the latter decomposes at 176°.

G. T. M.

**Reduction Products of  $\alpha$ - and  $\gamma$ -Benzylpyridines.** By A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 508–514).—By the reduction of 2- and 4-benzylpyridines with sodium in alcoholic

solution, yields of 60—70 per cent. of the corresponding benzyl piperidines are obtained.

i-2-Benzylpiperidine,  $\text{CH}_2\text{Ph}\cdot\text{C}_5\text{NH}_{10}$ , boils at  $267\text{--}268^\circ$  and crystallises in needles melting at  $32^\circ$ ; it has a faint odour resembling that of piperidine and is soluble in alcohol or ether; the *hydrochloride* forms hydrated, acicular crystals which melt at  $58^\circ$ , whilst the anhydrous salt melts at  $137^\circ$ ; the *platinichloride* crystallises from water in yellow needles which melt, with incipient blackening, at  $210^\circ$ ; the *aurichloride* separates as golden-yellow, flattened needles melting at  $168\text{--}170^\circ$ ; the *picrate* crystallises from alcohol or acetone in short, thick prisms which melt at  $156\text{--}157^\circ$  and are slightly soluble also in water or benzene.

4-Benzylpiperidine,  $\text{CH}_2\text{Ph}\cdot\text{C}_5\text{NH}_{10}$ , is a liquid having a faint odour of piperidine and boiling at  $279^\circ$ ; when strongly cooled, it yields a crystalline mass melting at  $6\text{--}7^\circ$ . It is soluble in alcohol or ether and has a sp. gr.  $0.9972$  at  $20^\circ/0^\circ$ . The *hydrochloride* forms white scales melting at  $172\text{--}173^\circ$ ; from aqueous solutions, the *platinichloride* separates in large, shining plates melting at  $197^\circ$ , the *aurichloride* in plates melting at  $145\text{--}146^\circ$ , and the *picrate* in long, thin, shining prisms melting at  $184^\circ$ .

4-Benzyltetrahydropyridine (4-benzylpiperidine),  $\text{CH}_2\text{Ph}\cdot\text{C}_5\text{NH}_8$ , which is also obtained from the reduction of 4-benzylpyridine, is a viscous liquid having an odour resembling that of sperm oil and boiling at  $280\text{--}282^\circ$ ; its sp. gr. is  $1.018$  at  $20^\circ/0^\circ$ . Its *picrate* separates from alcohol in thick prisms melting at  $129\text{--}131^\circ$ ; the *platinichloride* separates from water in yellow prisms melting at  $193\text{--}195^\circ$ .

The mother liquor from the reduction of the 2-compound also yields a small quantity of a liquid boiling at  $270\text{--}272^\circ$ , but there was not sufficient to allow of its investigation. T. H. P.

**Nitro- and Amino-stilbazoles.** By ERNST SCHMIDT (*Arch. Pharm.*, 1902, 240, 390).—The meta-compounds lately described (Feist, this vol., i, 642) had been obtained already by Schuftan (*Abstr.*, 1890, 1438). C. F. B.

**Action of p-Tolualdehyde on 2-Picoline and 2-Methyl-6-phenylpyridine.** By WOLFGANG DIERIG (*Ber.*, 1902, 35, 2774—2779).—p-Methyl-2-stilbazole,  $\text{C}_5\text{NH}_4\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\text{Me}$ , produced by condensing 2-picoline and p-tolualdehyde with zinc chloride at  $180^\circ$ , separates from dilute alcohol in colourless, felted crystals and melts at  $82^\circ$ ; it is insoluble in water, but dissolves in the ordinary organic solvents and forms a *hydrochloride*,  $\text{C}_{14}\text{H}_{13}\text{N}\cdot\text{HCl}\cdot\text{H}_2\text{O}$ , crystallising from water or alcohol in pale yellow needles sintering at  $170^\circ$  and melting at  $190\text{--}191^\circ$ . The *platinichloride*,  $(\text{C}_{14}\text{H}_{13}\text{N})_2\cdot\text{H}_2\text{PtCl}_6\cdot\text{H}_2\text{O}$ , decomposes at  $194\text{--}195^\circ$ ; the *aurichloride* crystallises in flattened, red needles decomposing at  $180\text{--}181^\circ$ ; the *mercurichloride* forms yellow needles blackening at  $219^\circ$  and decomposing at  $225^\circ$ ; the *picrate* separates in yellow needles and melts at  $193\text{--}194^\circ$ . A bromine additive product,  $\text{C}_{14}\text{H}_{13}\text{NBr}_2\cdot\text{HBr}$ , is obtained in the form of its hydrobromide by

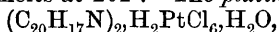
mixing bromine and the base in carbon disulphide solution; it decomposes at  $170^{\circ}$ .

*p*-Methyldihydro-2-stilbazole,  $C_5NH_4 \cdot CH_2 \cdot CH_2 \cdot C_6H_4Me$ , prepared by heating the preceding base with concentrated hydriodic acid at  $140$ — $150^{\circ}$ , is a colourless oil boiling at  $294$ — $296^{\circ}$  under the ordinary pressure; it has a neutral reaction and is darkened by exposure to light. The *platinichloride* and *aurichloride* crystallise in yellow needles and melt respectively at  $180^{\circ}$  and  $138$ — $140^{\circ}$ .

*p*-Methyl-2-stilbazoline,  $C_{14}H_{21}N$ , resulting from the action of sodium and alcohol on *p*-methyl-2-stilbazole, is an oil boiling at  $145$ — $148^{\circ}$  under 11 mm. pressure and having a characteristic, disagreeable odour. The *platinichloride*, *aurichloride*, and *picrate* crystallise in yellow needles melting respectively at  $182^{\circ}$ ,  $136^{\circ}$ , and  $125^{\circ}$ .

*p*-Tolyl-2-picolylalkine,  $C_6NH_4 \cdot CH_2 \cdot CH(OH) \cdot C_6H_4Me$ , resulting from the action of *p*-tolualdehyde on 2-picoline at  $140^{\circ}$ , crystallises from alcohol in lustrous needles melting at  $93^{\circ}$ ; the *platinichloride* is a red, crystalline substance sintering at  $140^{\circ}$  and melting at  $150^{\circ}$ ; the *aurichloride* forms golden-yellow needles soluble in water or alcohol, but not in ether; it melts at  $131^{\circ}$ .

6-Phenyl-*p*-methyl-2-stilbazole,  $C_5NH_3Ph \cdot CH \cdot CH \cdot C_6H_4Me$ , prepared by condensing 6-phenyl-2-methylpyridine and *p*-tolualdehyde with zinc chloride at  $180$ — $190^{\circ}$ , crystallises from alcohol in needles and from ether in thick spicules; it melts at  $113^{\circ}$ . The *hydrochloride*,  $C_{20}H_{17}N, HCl, H_2O$ , separates in yellow needles from water or alcohol; it sinters at  $195^{\circ}$  and melts at  $202^{\circ}$ . The *platinichloride*,



the *aurichloride*, and the *mercurichloride* crystallise in needles, and the last of these salts melts at  $183^{\circ}$ . The *picrate* crystallises with  $3H_2O$  and melts at  $196^{\circ}$ ; the bromine *additive* compound separates from alcohol in transparent leaflets and melts at  $173^{\circ}$ .

6-Phenyl-*p*-methyl-2-stilbazoline, produced by reducing the preceding base with sodium and alcohol, is a pale yellow oil having a disagreeable odour and boiling at  $245^{\circ}$  under 20 mm. pressure which solidifies to a glistening mass in a freezing mixture. The *hydrochloride* separates in white crystals soluble in water or alcohol; it sinters at  $230^{\circ}$  and melts at  $250^{\circ}$ ; the *picrate* crystallises in needles sintering at  $180^{\circ}$  and melting at  $197^{\circ}$ .

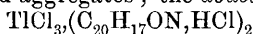
G. T. M.

**Action of Aldehydes on 6-Phenyl-2-methylpyridine.** By OTTO OLLENDORFF (*Ber.*, 1902, **35**, 2782—2786. Compare Abstr., 1901, i, 165; this vol., i, 234 and 818).—6-Phenyl-2-picolyl-*p*-nitrophenylalkine,  $C_5NH_3Ph \cdot CH_2 \cdot CH(OH) \cdot C_6H_4 \cdot NO_2$ , produced by condensing 6-phenyl-2-methylpyridine, *p*-nitrobenzaldehyde, and a small quantity of water at  $140^{\circ}$ , crystallises from alcohol in white needles and melts at  $112^{\circ}$ ; the *hydrochloride*,  $C_{19}H_{16}O_3N_2, HCl, H_2O$ , separates in tabular crystals from its alcoholic solution on adding hydrochloric acid; it melts at  $126^{\circ}$ . The *platinichloride* forms yellow prisms and melts at  $212^{\circ}$ .

6-Phenyl-2-*p*-nitrostilbazole,  $C_5NH_3Ph \cdot CH \cdot CH \cdot C_6H_4 \cdot NO_2$  crystallises from alcohol in lustrous plates melting at  $142^{\circ}$ ; it is obtained in small quantity by condensing 6-phenyl-2-methylpyridine and *p*-nitrobenz-

aldehyde at  $150^{\circ}$  in the presence of zinc chloride. The *hydrochloride* crystallises in white needles and melts at  $135^{\circ}$ .

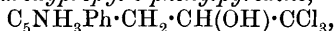
6-Phenyl-2-p-methoxystilbazole,  $C_5NH_3Ph \cdot CH:CH \cdot C_6H_4 \cdot OMe$ , prepared in a similar manner from the substituted pyridine base and anisaldehyde, crystallises in white needles and melts at  $129^{\circ}$ ; the *hydrochloride* separates in yellow needles melting at  $200^{\circ}$ , the hydrobromide is obtained in fan-shaped aggregates; the double thallic salt,



(compare Renz, this vol., i, 822), crystallises from dilute alcohol in yellow leaflets melting at  $98^{\circ}$ ; the *platinichloride* crystallises in prisms melting at  $245^{\circ}$  and the *mercurichloride* in yellow needles melting at  $221^{\circ}$ .

The preceding stilbazole derivative, when reduced with sodium and alcohol, yields an oily base which is characterised by its *hydrochloride*,  $C_{20}H_{25}ON, HCl$ , a substance crystallising in needles melting at  $229^{\circ}$ .

2- $\omega$ -Trichloro- $\beta$ -hydroxypropyl-6-phenylpyridine,

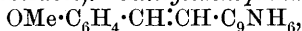


produced by heating 6-phenyl-2-methylpyridine with chloral on the water-bath, crystallises in triclinic plates melting at  $65^{\circ}$  and containing  $1\frac{1}{2}H_2O$ ; its *platinichloride*,  $(C_{14}H_{12}ONCl_3)_2, H_2PtCl_6, 2H_2O$ , crystallises in red needles and melts at  $201^{\circ}$ .

6-Phenyl-2-pyridylacrylic acid,  $C_5NH_3Ph \cdot CH:CH \cdot CO_2H$ , results from the action of alcoholic potassium hydroxide on the preceding base and is isolated in the form of its hydrochloride; the *platinichloride*,  $(C_{14}H_{11}O_2N)_2, H_2PtCl_6$ , crystallises from alcohol in yellow leaflets and melts at  $204^{\circ}$ .

G. T. M.

Action of Anisaldehyde on Quinaldine, 2-Picoline, and 2-Methyl-5-ethylpyridine. By O. BIALON (*Ber.*, 1902, 35, 2786–2790. Compare preceding abstracts).—*Anisylidenequinaldine*,



produced by condensing quinaldine and anisaldehyde at  $180^{\circ}$  in the presence of zinc chloride, crystallises from alcohol in white, lustrous leaflets melting at  $126^{\circ}$ ; the *hydrochloride* separates from water in yellow needles and melts at  $208^{\circ}$ ; the *platinichloride* is a yellow, insoluble substance melting at  $254^{\circ}$ ; the *aurichloride* is also yellow, crystallises from dilute hydrochloric acid and melts at  $199^{\circ}$ ; the *picrate* crystallises from acetone in yellow needles. When reduced with sodium and alcohol, the preceding base gives rise to p-methoxybenzyltetrahydroquinaldine,  $OMe \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot C_9NH_{10}$ , a secondary amine crystallising from alcohol in white, silky needles melting at  $71^{\circ}$ ; the benzoyl derivative, prepared by the Schotten-Baumann reaction, crystallises in white needles and melts at  $97^{\circ}$ ; the *hydrochloride* separates in yellow, feathery crystals and melts at  $218^{\circ}$ , the *aurichloride* and *platinichloride* are unstable.

p-Methoxy-2-stilbazole,  $OMe \cdot C_6H_4 \cdot CH:CH \cdot C_5NH_4$ , obtained in a poor yield by heating  $\alpha$ -picoline and anisaldehyde at  $180$ – $190^{\circ}$  for 36 hours in the presence of zinc chloride, crystallises from alcohol in lustrous, silvery leaflets melting at  $75^{\circ}$ ; the *hydrochloride* separates from hot water in yellow needles and melts at  $200$ – $201^{\circ}$ ; the *auri-*

*chloride* and *platinichloride* melt respectively at 178° and 225° (compare Schluftan, Abstr., 1889, 1437). On reduction with sodium and alcohol, the preceding base yields an oily *amine*, the hydrochloride of which crystallises in white needles and melts at 173°; the double salts with platinum, gold, and mercury are unstable, oily products.

*p*-Methoxy-5-ethyl-2-stilbazole,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{C}_5\text{NH}_3\text{Et}$ , resulting from the interaction of 2-methyl-5-ethylpyridine and anisaldehyde, was only isolated in the form of *aurichloride* and *platinichloride*, these salts melting respectively at 137° and 201°; the latter crystallises in yellow needles. G. T. M.

**Compounds of Quinoline and isoQuinoline with Cupric and Cuprous Thiocyanates.** By FRANZ M. LITTERSCHEID (*Arch. Pharm.*, 1902, 240, 386—390. Compare Abstr., 1901, i, 635; this vol., i, 308).—Quinoline and *isoquinoline* unite with dry cupric thiocyanate, forming green *substances* of the composition  $\text{Cu}(\text{C}_9\text{NH}_7 \cdot \text{CNS})_2$ .

With cuprous thiocyanate, they unite to form golden-yellow *crystals* with the composition  $\text{Cu}_2(\text{C}_9\text{NH}_7 \cdot \text{CNS})_2 \cdot 2\text{C}_9\text{NH}_7$ . When dried at 100°, these leave, first, lemon-yellow *substances* with the composition  $\text{Cu}_2(\text{C}_9\text{NH}_7 \cdot \text{CNS})_2$ , and finally cuprous thiocyanate.

With cuprosocupric thiocyanate, the golden-yellow crystals mentioned above were obtained. C. F. B.

**Preparation and Properties of some Quinoline Bases of Fluorene and Fluorenone.** II. By OTTO DIELS and OTTO STAEHLIN (*Ber.*, 1902, 35, 3275—3284. Compare Abstr., 1901, i, 521).—2-Aminofluorene (*loc. cit.*), when boiled with glycerol, arsenic acid, and concentrated sulphuric acid, gives *fluorenequinoline*,  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{C}_6\text{H}_4 \end{array} > \text{C}_9\text{NH}_7$ ,

which crystallises in white plates, melts at 134.5° (corr.), boils at 390—400°, and is almost insoluble in water or cold alcohol, but soluble in hot alcohol, methyl alcohol, benzene, or acetone; it is only when fresh that it dissolves in ether, but it easily dissolves in chloroform. The *hydrochloride* forms yellow needles containing  $2\text{H}_2\text{O}$  and melting at 110°, or when anhydrous at 241° (corr.). The salts are in general fairly insoluble. The *methiodide*,  $\text{C}_{17}\text{H}_{14}\text{NI} \cdot \text{H}_2\text{O}$ , when anhydrous, decomposes at 241° (corr.) without melting. When reduced with zinc and hydrochloric acid, the quinoline base gives *fluorenetetrahydroquinoline*,  $\text{C}_{16}\text{H}_{15}\text{N}$ , which forms white needles, melts at 143° (corr.), is insoluble in cold water, slightly soluble in alcohol to a blue fluorescent solution, and easily so in ether, acetone, benzene, or chloroform. Its hydrochloride crystallises well, as do also the sulphate, nitrate, and platinichloride. With oxidising agents, the tetrahydro-compound gives an indigo-blue coloration, which becomes violet, then brown; it reduces an ammoniacal silver solution. Nitrous acid converts it into a nitroso-compound of the formula  $\text{C}_{16}\text{H}_{14}\text{ON}_2$ . This nitrosoamine melts at 162° (corr.) and is insoluble in water, but soluble in chloroform, acetone, or benzene, or in concentrated sulphuric acid to a greenish solution; it responds to the Liebermann nitroso-reaction. The *phenylcarbimide* of the tetrahydro-base,  $\text{C}_{25}\text{H}_{20}\text{ON}_2$ , melts at 208°.

Fluorenequinoline, when oxidised with sodium dichromate and acetic

acid, gives a new base which forms yellow crystals, melts at  $191^{\circ}$  (corr.), and has the formula  $C_{16}H_9ON$ . This is insoluble in cold water or alcohol, but easily soluble in benzene or chloroform. Its *hydrochloride*, *sulphate*, and *nitrate* have been prepared.

2-Aminofluorenone, when boiled with glycerol, arsenic acid, and concentrated sulphuric acid, gives *fluorenonequinoline*, which crystallises in yellow needles and melts at  $188^{\circ}$ . The *methiodide*,  $C_{17}H_{12}ON \cdot H_2O$ , is insoluble in all organic solvents and decomposes when heated at  $240^{\circ}$ .

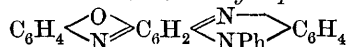
When fluorenonequinoline is fused with potassium hydroxide, the potassium salt of a carboxylic acid of the formula  $C_{15}H_{10}N \cdot CO_2H$  is obtained. The free acid can be crystallised from hot alcohol, melts at  $264$ — $265^{\circ}$  (corr.), and is insoluble in water, ether, chloroform, or acetone, but is soluble in solutions of acids or bases. J. McC.

**Some Ammonium Compounds. X. Hydroxyphenylmethyl-dihydroacridine.** By HERMAN DECKER, TH. HOCK, and C. DJIWONSKY (*Ber.*, 1902, **35**, 3068—3079. Compare *Abstr.*, 1893, i, 115; this vol., i, 691).—The *methyl ether* of 5-hydroxy-5-phenyl-10-methyl-5:10-dihydroacridine is formed when the carbinol base is boiled with methyl alcohol. It forms colourless needles which melt at  $152$ — $153^{\circ}$ , and become red. The corresponding *isobutyl ether* also forms colourless crystals which melt at  $108.5^{\circ}$ . Halogens act on hydroxyphenylmethyl-dihydroacridine, and with iodine the *di-iodide* of *phenylacridine methiodide* is produced, which crystallises from chloroform in dark, six-sided plates and melts at  $148$ — $150^{\circ}$ . With excess of iodine, a polyiodide is formed.

The action of methyl iodide on the carbinol base is to reproduce phenylacridine methiodide.

From a consideration of the work of Werner, Kehrman, and others, the authors deduce support for the theories which Decker has already advanced for the constitution and mode of formation of these ammonium compounds. J. McC.

**Oxidation Products of o-Aminophenol.** By EMIL DIEFOLDER (*Ber.*, 1902, **35**, 2816—2822).—When *o*-aminophenol hydrochloride is oxidised with potassium ferricyanide or ferric chloride, a mixture of triphenodioxazine and 3-hydroxybenzeneazoxindone is obtained. 3-Hydroxybenzeneazoxindone,  $C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown N \end{smallmatrix} \begin{smallmatrix} \diagup O \\ \diagdown N \end{smallmatrix} C_6H_2 \cdot OH$ , which is the tautomeric form of phenoxazine-2:3-quinone, crystallises from xylene in beautiful, brown needles with a blue iridescence, blackens at  $240$ — $250^{\circ}$ , and decomposes at  $278^{\circ}$ ; it is soluble in ammonia and when treated with sodium hydroxide yields *o*-aminophenol and dihydroxyquinone. The *acetyl* derivative crystallises in clusters of golden, lustrous leaflets and melts at  $225$ — $226^{\circ}$ . An insoluble by-product which decomposed at  $268^{\circ}$ , obtained in the above oxidation, was proved to be a double compound of 3-hydroxybenzeneazoxindone and 3-aminobenzeneazoxindone. 7-Phenyltriphenazineoxazine,





(Abstr., 1898, i, 93) crystallises from nitrobenzene and is identical with the compound wrongly described as N-methyltriphenazinooxazine-carbazole (Abstr., 1901, i, 618).

A red coloration with ferric chloride, which is converted into blue or green with reducing agents such as stannous chloride, seems to be characteristic for those *o*-aminophenols which have two free para-positions, and not more than one alkyl in the amino-group.

R. H. P.

### Aminohydroxydiphenylamine and Analogous Compounds.

By ROBERT GNEHM [with H. BOTS and G. WEBER] (*Ber.*, 1902, 35, 3085—3088).—By the condensation of dimethyl-*p*-phenylenediamine with quinol or by the reduction of phenol-blue, *dimethyl-p-amino-p-hydroxydiphenylamine* is obtained in the form of white needles which melt at 161°. Its *diacetyl* derivative melts at 131° and its *dibenzoyl* derivative at 210°. When treated with concentrated nitric acid, the diacetyl compound loses the acetyl groups and a *tetranitro*-compound melting at 228° is formed. With methyl iodide or ethyl iodide, direct addition takes place and well crystallised products melting at 218° and 206° respectively are obtained.

When resorcinol is used in place of quinol, *dimethyl-p-amino-m-hydroxydiphenylamine* is formed; this is easily soluble in the common organic solvents or in hot water and melts at 99°. It forms a *diacetyl* compound which melts at 101° and a *dibenzoyl* derivative which melts at 112°. With nitrous acid, it gives a *nitrosoamine*, which separates from dilute alcohol in brownish needles and melts at 125·5°.

By the reduction of indamine, *dimethyl-p-diaminodiphenylamine* is formed. It is soluble in hot water and melts at 116°.

2-*p*-Dimethylanilino-7-hydroxynaphthalene,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$ , is produced from dimethyl-*p*-phenylenediamine and 2:7-dihydroxynaphthalene; it crystallises in white plates and melts at 126—127°.

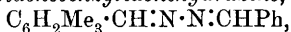
J. McC.

**Benzylidenehydrazine.** By THEODOR CURTIUS and H. FRANZEN (*Ber.*, 1902, 35, 3234—3239).—Benzylidenehydrazine,  $\text{CHPh} \cdot \text{N} \cdot \text{NH}_2$  (Curtius and Pflug, Abstr., 1892, 456), is best prepared by the action of hydrazine on benzaldazine,  $\text{CHPh} \cdot \text{N} \cdot \text{N} \cdot \text{CHPh}$ . The *picrate*,  $\text{CHPh} \cdot \text{N} \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{OH}$ , separates as a thick, yellow precipitate and is sparingly soluble in all solvents. It condenses with phenylthiocarbimide to form benzylidenephénylthiosemicarbazide,  $\text{CHPh} \cdot \text{N} \cdot \text{NH} \cdot \text{CS} \cdot \text{NHPh}$  (Pulvermacher, Abstr., 1894, i, 304), and with acetic anhydride gives acetylbenzylidenehydrazine (Curtius and Schäfer, Abstr., 1895, i, 263), whilst ethyl bromide converts it into hydrazine hydrobromide and benzaldazine.

*o*-Hydroxybenzylidenehydrazine (Cajar, Abstr., 1899, i, 146) can be prepared in a similar manner from the azine; the *picrate* forms a yellow, slightly soluble, crystalline powder. *o*-Hydroxybenzylidenephénylthiosemicarbazide,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \cdot \text{NH} \cdot \text{CS} \cdot \text{NHPh}$ , separates from alcohol in white flakes or needles.

2:4:5-Trimethylbenzylidenehydrazine,  $\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{CH} \cdot \text{N} \cdot \text{NH}_2$ , from 2:4:5-trimethylbenzaldazine (Graf, *Diss.*, Heidelberg, 1899), boils

at 165—166° under 14 mm. pressure, solidifies in the receiver, melts at 70°, and dissolves readily in organic solvents; the *picrate* is a yellow, slightly soluble, crystalline powder and melts at 170—171°; 2:4:5-trimethylbenzylidenbenzylidenehydrazine,



separates from alcohol in yellow needles; the *o*-hydroxybenzylidenehydrazine,  $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CH}\cdot\text{N}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , crystallises from alcohol in yellow needles.

*p*-Methylbenzylidenehydrazine,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}\cdot\text{N}\cdot\text{N}\cdot\text{NH}_2$ , is a white, crystalline substance, boils at 148° under 12 mm. pressure, and melts at 56°; the *picrate* is a yellow, crystalline powder and melts at 175—176°.

*p*-Methylbenzylidenbenzylidenehydrazine,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}\cdot\text{N}\cdot\text{N}\cdot\text{CHPh}$ , separates from alcohol in yellow needles.

*m*-Chlorobenzylidenehydrazine,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}\cdot\text{N}\cdot\text{N}\cdot\text{NH}_2$ , is a white, crystalline substance and boils at 163—164° under 20 mm. pressure; the *benzylidenehydrazine*,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}\cdot\text{N}\cdot\text{N}\cdot\text{CHPh}$ , separates from alcohol in yellow needles.

T. M. L.

**Preparation of Hydrazides from Diammonium Salts.** By THEODOR CURTIUS and H. FRANZEN (*Ber.*, 1902, 35, 3239—3241).—Hydrazides can be prepared in good yield by directly heating the hydrazine salts of the acids; the preparation of acetyl-, propionyl-, lactyl-, and benzoyl-hydrazines by this method is described.

*Hydrazine p*-bromobenzoate,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{H}\cdot\text{N}_2\text{H}_4$ , separates from alcohol in colourless needles, softens at 165°, melts at 170°, and dissolves readily in alcohol or water. When heated, it is converted into *di*-*p*-bromobenzoylhydrazine,  $\text{N}_2\text{H}_2(\text{CO}\cdot\text{C}_6\text{H}_4\text{Br})_2$ , which crystallises from alcohol in minute, colourless needles and melts at 280°; *p*-bromobenzoylhydrazine was not produced.

*Hydrazine p*-toluate,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}\cdot\text{N}_2\text{H}_4$ , forms colourless, soluble needles, and when heated is converted into a mixture of *p*-toluoylhydrazine and *p*-ditoluoylhydrazine.

T. M. L.

**Constitution of the Alkyl Derivatives of Methyluracil and 8-Methyluric Acid.** By ROBERT BEHREND and RICHARD THURM (*Annalen*, 1902, 323, 160—178. Compare *Abstr.*, 1900, i, 63).—The dimethyluracils are most conveniently prepared by methylating 4-methyluracil with less than the calculated quantities of methyl iodide and potassium hydroxide; under these conditions, the mixture of dimethyl derivatives contains 60 per cent. of the  $\beta$ -compound and 40 per cent. of the  $\alpha$ -isomeride, the formation of trimethyluracil being reduced to a minimum.

Both these compounds, on further methylation, yield the same trimethyl derivative, namely, 1:3:4-trimethyluracil; this compound separates in rhombic crystals melting at 110—112°; like the monomethyl compound, it may be sublimed without decomposition.

The two dimethyl derivatives, on oxidation, give rise to the same methyloxaluric acid, the products of the two reactions being shown to be crystallographically identical. The following results indicate that  $\alpha$ -dimethyluracil is 3:4-dimethyl-2:6-dioxypyrimidine, whilst its  $\beta$ -isomeride is 1:4-dimethyl-2:6-dioxypyrimidine.

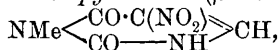
3:4-Dimethyl-1-ethyluracil (3:4-dimethyl-1-ethyl-2:6-dioxypyrimidine,

$\text{NEt} \begin{smallmatrix} \text{CO} - \text{CH} \\ \text{CO} - \text{NMe} \end{smallmatrix} \text{CMe}$ , produced by ethylating  $\alpha$ -dimethyluracil with ethyl iodide or bromide, crystallises from benzene in lustrous leaflets melting at  $112-114^\circ$ .

1:4-Dimethyl-3-ethyluracil (1:4-dimethyl-3-ethyl-2:6-dioxypyrimidine),  $\text{NMe} \begin{smallmatrix} \text{CO} - \text{CH} \\ \text{CO} - \text{NEt} \end{smallmatrix} \text{CMe}$ , prepared in a similar manner from  $\beta$ -dimethyluracil, crystallises from alcohol in prisms and melts at  $110-112^\circ$ .

1-Methyl-2:6-dioxy-5-nitropyrimidine-4-carboxylic acid ( $\beta$ -methylnitro-uracilcarboxylic acid),  $\text{NMe} \begin{smallmatrix} \text{CO} - \text{C}(\text{NO}_2) \\ \text{CO} - \text{NH} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{H}$ , is produced by oxidising  $\beta$ -dimethyluracil with a mixture of sulphuric and nitric acids, the latter being saturated with nitrous fumes; it separates from water in light yellow crystals containing  $2\text{H}_2\text{O}$ . The water of crystallisation is evolved at  $100^\circ$ , and carbon dioxide is eliminated at  $140-150^\circ$ . The double salt,  $2\text{C}_6\text{H}_4\text{O}_6\text{N}_3\text{K} \cdot \text{KNO}_3 \cdot 2\text{H}_2\text{O}$ , separates in feathery crystals when the crude product of oxidation is neutralised with potassium hydroxide. The simple salt,  $\text{C}_6\text{H}_4\text{O}_6\text{N}_3\text{K} \cdot \text{H}_2\text{O}$ , separates in yellow crystals from an aqueous solution of the preceding compound. The crude acid also contains a less soluble substance,  $\text{C}_6\text{H}_4\text{O}_5\text{N}_4$ , which dissolves in hot water, yielding an acid solution which develops an intense yellow coloration with the alkalis.

1-Methyl-2:6-dioxy-5-nitropyrimidine ( $\beta$ -methylnitrouracil),



produced on heating the preceding acid, crystallises from water in colourless needles and melts at  $263^\circ$  with partial decomposition; its potassium derivative is obtained by heating the potassium salt of the preceding acid.

1-Methyl-3-ethyl-2:6-dioxy-5-nitropyrimidine (1-methyl-3-ethylnitro-uracil),  $\text{NMe} \begin{smallmatrix} \text{CO} - \text{C}(\text{NO}_2) \\ \text{CO} - \text{NEt} \end{smallmatrix} \text{CH}$ , obtained by heating the silver derivative of the preceding compound with ethyl iodide at  $100^\circ$ , crystallises from water in prismatic needles and melts at  $105-106^\circ$ ; this substance is identical with the product formed by successively ethylating and methylating the potassium derivative of nitrouracil.

3-Methyl-1-ethyl-2:6-dioxy-5-nitropyrimidine (3-methyl-1-ethylnitro-uracil),  $\text{NEt} \begin{smallmatrix} \text{CO} - \text{C}(\text{NO}_2) \\ \text{CO} - \text{NMe} \end{smallmatrix} \text{CH}$ , prepared from  $\alpha$ -methylnitrouracil, crystallises from water in needles melting at  $124^\circ$ ; it is decomposed, on prolonged heating, in aqueous or alcoholic solution; Lehmann, who first obtained the two preceding dialkylated nitrouracils, gave the melting point of the former as  $70-73^\circ$  and that of the latter as  $106-109^\circ$  (compare Abstr., 1890, 33).

$\alpha$ -Dimethyluracil can be successively converted into 3-methylnitrouracil, 3-methylisobarbituric acid, 3-methylisodialuric acid, and  $\delta$ -methyluric acid. If, therefore, the original substance is 3:4-dimethyl-2:6-dioxypyrimidine, the final product must contain its methyl group in position 3 of the pyrimidine ring, and this cycle of changes supplies confirmatory evidence in support of Fischer's view that the acid in question is 3-methyluric acid.

G. T. M.

**Oxidation of Methyluracil.** By ROBERT BEHREND and RICHARD GRÜNEWALD (*Annalen*, 1902, 323, 178—204. Compare preceding abstract).—When methyluracil is oxidised with an amount of potassium permanganate equivalent to three atoms of oxygen, acetylcarbamide and oxaluric acid are produced, the relative proportion of these substances depending on the temperature; in the cold, the former compound is the chief product, at the boiling point, the latter predominates, whilst the two are formed in approximately equal amounts at 40—50°. This result is obtained, however, only in alkaline solutions; if the mixture becomes neutral or acid, the proportion of acetylcarbamide increases and predominates even at high temperatures.

*3-Hydroxy-4-methyluracil*,  $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{C}(\text{OH}) \\ \text{CO} \text{---} \text{NH} \end{smallmatrix} \text{CMe}$ , is produced when 4-methyluracil is oxidised with one atomic proportion of oxygen by means of permanganate solution, the maximum yield being obtained at 20—40°, when the solution is rendered neutral by the addition of an equivalent amount of acetic acid. The substance is sparingly soluble in water or alcohol, but readily dissolves in alkaline or ammoniacal solutions; it forms prismatic, anisotropic crystals having either pyramidal or truncated ends; with neutral ferric chloride, it develops an intense blue coloration which disappears after a time, or more rapidly on warming or treating with acids or alkalis. The compound was not obtained in a state of purity, the percentage of carbon being somewhat too high.

*3-Acetoxy-4-methyluracil*, produced by treating the preceding substance with acetic anhydride, crystallises from water in felted needles decomposing at 238—241°; it regenerates the hydroxy-compound by alkaline hydrolysis. *3-Hydroxy-4-methyluracil*, on further oxidation, gives rise to acetylcarbamide and oxaluric acid.

Although a compound intermediate between 3-hydroxy-4-methyluracil and its oxidation products could not be isolated, yet the soluble product, obtained by treating 3:3-dibromo-4-hydroxy-4-methyluracil,  $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CBr}_2 \\ \text{CO} \text{---} \text{NH} \end{smallmatrix} \text{CMe} \cdot \text{OH}$ , with potassium hydroxide solution, appears to contain such a substance, namely, 3:3:4-trihydroxy-4-methyldihydrouracil,  $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{C}(\text{OH})_2 \\ \text{CO} \text{---} \text{NH} \end{smallmatrix} \text{CMe} \cdot \text{OH}$ , for on reduction it yields 3-hydroxy-4-methyluracil, whilst on oxidation acetylcarbamide and oxaluric acid are produced. Acetylallanturic acid is probably an intermediate product of the latter process, but it has not been isolated.

This supposition derives support from the fact that in acid or neutral solutions oxidation by chromic or permanganic acid leads to the formation of parabanic acid, a substance which should readily result from the hypothetical compound,  $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{C}(\text{OH}) \cdot \text{CO} \cdot \text{CH}_3 \\ \text{CO} \text{---} \text{NH} \end{smallmatrix} + \text{O} =$   
 $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CO} \\ \text{CO} \text{---} \text{NH} \end{smallmatrix} + \text{CH}_3 \cdot \text{CO}_2\text{H}.$

The production of the same methyloxaluric acid from  $\alpha$ - and  $\beta$ -dimethyluracils may be explained by supposing that the oxidation follows a course similar to that just indicated, the two isomerides

giving rise successively to methyl derivatives of trihydroxymethyl-dihydrouracil and acetyllallanturic acid, the latter substances yielding, by further oxidation, the same methylparabanic acid,  $\text{NMe} \begin{smallmatrix} \text{CO} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \end{smallmatrix}$ , from which methyloxaluric acid is finally obtained. G. T. M.

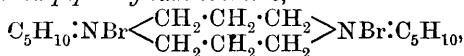
**Action of Mucobromic and Mucochloric Acids on Benzamidine.** By FRANZ KUNCKELL and LEO ZUMBUSCH (*Ber.*, 1902, **35**, 3164—3168. Compare *Abstr.*, 1901, i, 759).—*Benzamidine 5-bromo-2-phenylpyrimidine-6-carboxylate*,  $\text{N} \begin{smallmatrix} \text{CH} \cdot \text{CBr} \\ \text{CPh} = \text{N} \end{smallmatrix} > \text{C} \cdot \text{CO}_2\text{H} \cdot \text{NH}_2 \cdot \text{CPh} \cdot \text{NH}$ , is obtained when a chloroform solution of mucobromic acid is left in contact with an excess of  $\alpha$ -benzamidine for some time, or more readily when the mixture is warmed. It is sparingly soluble in water and crystallises in colourless needles melting at  $228^\circ$ . The acid crystallises in needles, melts at  $159^\circ$ , and yields a barium salt,  $\text{C}_{22}\text{H}_{12}\text{O}_4\text{N}_4\text{Br}_2\text{Ba}$ , crystallising in long, colourless needles.

Bromine converts the acid into a compound,  $\text{C}_{11}\text{H}_6\text{O}_2\text{N}_2\text{Br}_2$ , and ammonia into 5-amino-2-phenylpyrimidine-6-carboxylic acid melting at  $196^\circ$ . The hydrochloride melts at  $183^\circ$ . When heated at  $165$ — $170^\circ$ , the acid readily loses carbon dioxide and yields 5-bromo-2-phenylpyrimidine, melting at  $104^\circ$ . Mucochloric acid and benzamidine yield benzamidine 5-chloro-2-phenylpyrimidine-6-carboxylate, melting at  $230$ — $231^\circ$ ; the acid melts at  $164^\circ$  and the barium salt crystallises in long needles. 5-Chloro-2-phenylpyrimidine melts at  $96^\circ$ . J. J. S.

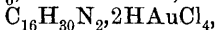
**Action of Benzamidine on  $\beta$ -Bromo- $\omega$ -benzylacetophenone.** By FRANZ KUNCKELL and O. SARFERT (*Ber.*, 1902, **35**, 3169).—2:4:6-Triphenyl-3:4-dihydropyrimidine,  $\text{N} \begin{smallmatrix} \text{CPh} \cdot \text{NH} \\ \text{CPh} \cdot \text{CH} \end{smallmatrix} > \text{CHPh}$ , is obtained when a chloroform solution of benzamidine is warmed with  $\beta$ -bromo- $\omega$ -benzylacetophenone (Rupe and Schneider, *Abstr.*, 1895, i, 361); it melts at  $186$ — $187^\circ$ , is readily soluble in chloroform, alcohol, or ether, and as a feeble base combines with hydrogen chloride in the absence of water. J. J. S.

**Cyclic Diammonium Compounds.** By MAX SCHOLTZ (*Ber.*, 1902, **35**, 3047—3055).—The stability of cyclic compounds containing nitrogen in the ring is discussed, and the author has prepared the following compounds containing two nitrogen atoms from dipiperidylethane and dipiperidylpropane by the action of methylene iodide, ethylene bromide, trimethylene bromide, and *o*-, *m*-, and *p*-xylylene bromides. With the exception of methylene iodide, these dihalogen compounds give diammonium derivatives, as has been proved by the analysis of the platinichlorides and aurichlorides. *Ethylenetrimethylenedipiperidylum bromide*,  $\text{C}_5\text{H}_{10} \cdot \text{NBr} \begin{smallmatrix} \text{CH}_2 \text{---} \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{NBr} \cdot \text{C}_6\text{H}_{10}$ , obtained by the action of trimethylene bromide on dipiperidylethane, is easily soluble in water and crystallises in rhombic plates.

*Ditrimethylenedipiperidylum bromide*,

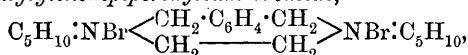


obtained from dipiperidylpropane and trimethylene bromide at the ordinary temperature as a flaky mass, volatilises at 100°. The *platinichloride*,  $C_{16}H_{30}N_2 \cdot H_2PtCl_6$ , melts at 259°, and the *aurichloride*,



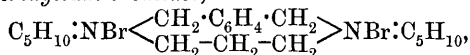
at 214°.

*Ethylene-o-xylylenedipiperidylum bromide*,



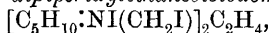
which is obtained from dipiperidylethane and *o*-xylylene bromide in chloroform solution, can be separated from alcoholic solution by means of ether as a hygroscopic, crystalline powder. The *platinichloride* does not melt but decomposes at 300°; the *aurichloride* melts at 243°. The corresponding meta- and para-compounds are similarly obtained. The *platinichloride* of the meta-compound melts at 262°, the *aurichloride* at 182°; the *platinichloride* of the para-compound melts at 235°, the *aurichloride* at 210°.

From dipiperidylpropane and the xylylene bromides, *trimethylene-xylylenedipiperidylum bromides*,

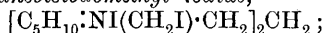


are formed. The *platinichloride* of the ortho-compound melts at 242—243°, and the *aurichloride* at 141°. The *platinichloride* of the para-compound melts at 252°, and the *aurichloride* becomes dark at 140° and melts at 200°.

By the action of methylene iodide on dipiperidylethane and dipiperidylpropane, two mols. of the iodide combine with one mol. of the base with formation of *dipiperidylethanebisiodomethyl iodide*,



and *dipiperidylpropanebisiodomethyl iodide*,



the former crystallises in yellow plates, is insoluble in ether, and melts at 182°; the latter forms yellow crystals, melts at 195—196°, and is sparingly soluble in alcohol or water, and insoluble in ether.

J. McC.

### Synthesis of Xanthine Derivatives by means of *p*-Nitrophenol.

By WALTHER BORSCHÉ (*Chem. Centr.*, 1902, ii, 284—285; from *Nachr. k. Ges. Wiss. Göttingen*, 1902, 141—145. Compare Störmer, *Abstr.*, 1901, i, 726).—*Dinitrodihydroxymethylxanthine*,  $C_{15}H_{12}O_7N_2$ , obtained in almost theoretical quantity by the action of formaldehyde on *p*-nitrophenol in presence of dilute sulphuric acid at 40°, separates from alcohol in colourless crystals, melts at 148°, is insoluble in alkalis, and when warmed with nitric acid yields picric acid. By the action of potassium permanganate and chromic acid, nitrosalicyclic acid and 2 : 7-dinitroxanthine-4 : 5-dicarboxylic acid,  $C_{15}H_8O_9N_2$ , are formed respectively. The latter crystallises from alcohol in slightly yellow needles, melts at 110°, and is dissolved and decomposed by alkali hydroxides or carbonates with formation of formaldehyde and the alkali salt of 5-nitrosalicyclic acid; 3-nitro-6-hydroxybenzyl alcohol is probably an intermediate product of the reaction.

*o*-Nitrophenol is not attacked by formaldehyde.

E. W. W.

**Triketones. II.  $\beta\gamma\delta$ -Triketo- $\delta$ -phenylbutane.** By FRANZ SACHS and ALFRED RÖHMER (*Ber.*, 1902, 35, 3307—3319. Compare *Abstr.*, 1901, i, 670).—The preparation of  $\beta\gamma\delta$ -triketopentane has been improved and is described in detail. It gives a yellowish-red to brown coloration with sulphuric acid and benzene containing thiophen; further, it does not form insoluble compounds with sodium sulphite or hydrogen sulphite; both it and its hydrate have a bitter, burning taste and colour the human skin brown. The free keto-group in the *bisphenylhydrazone* (*loc. cit.*) does not react with phenylhydrazine in alcoholic solution or with semicarbazide. The constitution of the 2-acetyl-3-methylquinoxaline previously obtained from the triketopentane and *o*-phenylenediamine hydrochloride is confirmed by the formation of the *phenylhydrazone*,  $C_6H_4 \begin{smallmatrix} \text{N:C} \cdot CMe \cdot \text{N} \cdot NPh \\ \text{N:C} \cdot CMe \end{smallmatrix}$ , which crystallises

in small, lemon-coloured needles and melts at  $178^\circ$ , of the *oxime*, which melts at  $194.5^\circ$ , of the *p*-nitrophenylhydrazone, which melts at  $264^\circ$ , and of the *semicarbazone*, which crystallises from glacial acetic acid and melts at  $267$ — $268^\circ$ . The quinoxaline condenses with benzaldehyde in the presence of sodium ethoxide, forming 2:3-cinnamoylmethylquinoxaline,  $C_6H_4 \begin{smallmatrix} \text{N:C} \cdot CO \cdot CH \cdot CHPh \\ \text{N:C} \cdot CMe \end{smallmatrix}$ . The bis-*semicarbazone* of the triketopentane crystallises from glacial acetic acid, melts at  $221^\circ$ , dissolves in alkalis, and is reprecipitated by acids. Hydrazine hydrate reacts violently with triketopentane with the evolution of nitrogen and the formation of 4-hydroxy-3:5-dimethylpyrazole, which crystallises in colourless needles and melts at  $173.5^\circ$ .

$\beta\gamma\delta$ -Triketo- $\delta$ -phenylbutane can be prepared by analogous methods to those described (*loc. cit.*). The condensation product of benzoylacetone and *p*-nitrosodimethylaniline crystallises from alcohol in reddish-brown needles and melts at  $99^\circ$ . The *triketone*,  $COMe \cdot CO \cdot CPh$ , is a reddish-yellow oil, is insoluble in water, but miscible with all organic solvents, and is hygroscopic; it gives a violet coloration with sulphuric acid and benzene containing thiophen and reduces Fehling's solution. The *hydrate*,  $COMe \cdot C(OH)_2 \cdot CPh$ , forms colourless rhombic crystals, melts at  $54$ — $58^\circ$ , and is much more stable in air than the triketopentane. The  $\beta$ -phenylhydrazone crystallises in dark red, rhombic prisms, melts at  $167^\circ$ , and condenses with *o*-phenylenediamine, forming a compound,  $C_{22}H_{18}N_4$ , which melts at  $183^\circ$ . The triketone reacts with an excess of phenylhydrazine, forming 1:5-diphenyl-3-methylpyrazole-4-azobenzene,  $\begin{smallmatrix} NPh \\ | \\ CPh : C(N : NPh) \end{smallmatrix} \begin{smallmatrix} N \\ \text{N} \end{smallmatrix} \gg CMe$ , which crystal-

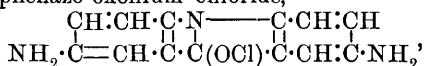
lises from alcohol and melts at  $136.5^\circ$ . The  $\beta$ -monosemicarbazone of the triketone crystallises in felted needles and melts at  $190^\circ$ . 2-Acetyl-3-phenylquinoxaline crystallises in colourless needles, melts at  $99.5^\circ$ , and forms a semicarbazone melting at  $243^\circ$  and a phenylhydrazone which melts at  $183^\circ$  and is identical with the product obtained from the phenylhydrazone of the ketone and *o*-phenylenediamine; the condensation product of benzaldehyde and the quinoxaline melts at  $164^\circ$ . 4-Hydroxy-5-phenyl-3-methylpyrazole crystallises in white needles and melts at  $188^\circ$ . An undetermined compound,

obtained by the polymerisation of the ketone in the presence of piperidine, crystallised in broad needles and melted at  $202^{\circ}$ . R. H. P.

**Preparation of Aromatic Guanidines.** By FREDERICK J. ALWAY and CAREY E. VAIL (*Amer. Chem. J.*, 1902, **28**, 158—164).—Aromatic guanidines are best prepared by Hofmann's method (*Ber.*, 1869, **2**, 458). The thiocarbamide and amine in molecular proportion are dissolved in alcohol and the solution is heated until it boils; an excess of lead hydroxide is then added and heating is continued until desulphurisation is complete. On the addition of nitric acid to the filtered solution, the nitrate slowly separates and may be collected and recrystallised. In the preparation of phenyldi-*o*-tolylguanidine, a small quantity of tri-*o*-tolylguanidine is simultaneously formed. The yield of the nitrate (or mixture of nitrates) amounts to 75—90 per cent. of the theoretical. The nitrates of the following bases have been obtained by the method described: diphenyl-*m*-tolyl-, phenyldi-*p*-tolyl-, *o*-tolyl-di-*p*-tolyl-, *m*-tolyl-di-*p*-tolyl-, di-*o*-tolyl-*p*-tolyl-, di-*o*-tolyl-*m*-tolyl-, and phenyl-*o*-tolyl-*p*-tolyl-guanidine.

Diphenyl-*p*-tolylguanidine nitrate is obtained in equally good yield from diphenylthiocarbamide and *p*-toluidine, and from phenyl-*p*-tolylthiocarbamide and aniline. It forms small, colourless plates and melts at  $196$ — $197^{\circ}$ . E. G.

**Dyes of the Capri-blue Group.** By RICHARD MÖHLAU, K. KLIMMER, and EDMUND KAHL (*Chem. Centr.*, 1902, ii, 377—378; 458—459; from *Zeit. Farb. Textilchem.*, 1902, **1**, 313—324, 354—356).—The following compounds are used in the preparation of dyes of the capri-blue or diaminophenazo-oxonium chloride,



group.

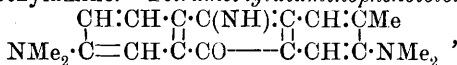
4-Nitro-2-dimethylaminotoluene,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NMe}_2$ , prepared by nitrating 2-dimethylaminotoluene in concentrated sulphuric acid, boils at  $280^{\circ}$  with partial decomposition and is readily soluble in acetic acid, mineral acids, or most organic solvents. 4-Amino-2-dimethylaminotoluene,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NMe}_2$ , obtained by reducing the preceding compound with tin and hydrochloric acid, is an oil, boils at  $248^{\circ}$  (uncorr.), is volatile in steam, and readily soluble in acids or organic solvents. The sulphate,  $\text{C}_9\text{H}_{14}\text{N}_2 \cdot \text{H}_2\text{SO}_4$ , separates from alcohol in lustrous crystals and melts at  $209^{\circ}$ ; the hydrochloride melts at  $208^{\circ}$ . The acetyl derivative,  $\text{NHAc} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NMe}_2$ , crystallises from light petroleum in needles, is readily soluble, and melts at  $103^{\circ}$ . 2-Dimethylamino-4-hydroxytoluene,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OH}$ , prepared from 4-amino-2-dimethylaminotoluene or by melting potassium 2-dimethylamino-4-sulphonic acid with potassium hydroxide, melts at  $46^{\circ}$ , boils at  $253^{\circ}$ , and is readily soluble in acids, alkalis, or organic solvents. The hydrochloride,  $\text{C}_9\text{H}_{13}\text{ON} \cdot \text{HCl}$ , forms rhombohedral crystals and melts at  $213^{\circ}$ . The acetyl derivative,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OAc}$ , is a readily soluble liquid and boils at  $195^{\circ}$  under 60 mm. pressure. The benzoyl derivative crystallises from alcohol in four-sided plates and melts at  $46^{\circ}$ . By the action of nitrous acid on 2-dimethylamino-4-hydroxytoluene in



aqueous solution in presence of excess of hydrochloric acid, dimethylamine and Kostanecki's 3:5-dinitrosocresorcinol,  $C_6HMeO_2(NO)_2$  (Abstr., 1888, 263) are formed. On the other hand, by the action of an aqueous solution of sodium nitrite on crystalline 2-dimethylamino-4-hydroxytoluene hydrochloride, a theoretical yield of 5-nitroso-2-dimethylamino-4-hydroxytoluene,  $NMe_2 \cdot C_6H_2Me(NO) \cdot OH$ , is obtained; it crystallises from benzene in reddish-brown needles, melts at  $102^\circ$ , and is readily soluble in alcohol, benzene, acetic acid, pyridine, or chloroform, and slightly so in water or ether. The *hydrochloride*,  $C_9H_{12}O_2N_2 \cdot HCl$ , melts at  $170^\circ$ , and the *sodium salt*,  $C_9H_{11}O_2N_2Na$ , forms a blood-red solution in water or alcohol.

The following compounds are prepared from 2-diethylaminotoluene or its derivatives. 4-Nitro-2-diethylaminotoluene is an oil, boils at  $283^\circ$  (uncorr.), and is volatile in steam. 4-Amino-2-diethylaminotoluene is a yellow oil which can be distilled at  $259^\circ$  in an atmosphere of carbon dioxide; the *hydrochloride*,  $C_{11}H_{18}N_2 \cdot 2HCl, H_2O$ , melts and decomposes at  $213-215^\circ$ . 2-Diethylamino-4-hydroxytoluene is a slightly yellow oil, becomes red on exposure to air, distils at  $259-261^\circ$  (uncorr.) in an atmosphere of carbon dioxide, and is volatile in steam; by allowing its solution in benzene to evaporate at the ordinary temperature, it separates in crystals which melt at  $46^\circ$ . The *hydrochloride*,  $C_{11}H_{17}ON \cdot HCl$ , crystallises from alcohol in rhombohedral crystals and melts at  $187^\circ$ . The *benzoyl* derivative crystallises from alcohol in rhombic prisms and melts at  $36^\circ$ . 2-Diethylaminotoluene-4-sulphonic acid,  $NEt_2 \cdot C_6H_3Me \cdot SO_3H, H_2O$ , crystallises from water in hexagonal, rhombic plates and is slightly soluble in cold water or alcohol. The *potassium salt* separates from 95 per cent. alcohol in crystals containing water of crystallisation.

*Tetramethyldiaminophenotolazo-oxonium chloride*,  $C_{17}H_{20}ON_3Cl$ , is prepared by treating 2-dimethylamino-4-hydroxytoluene with nitroso-dimethylaniline in boiling glacial acetic acid. The corresponding *iodide* crystallises from alcohol in violet needles, is slightly soluble in water, and more readily so in alcohol, acetone, or chloroform, forming greenish-blue solutions. By boiling an aqueous solution with alkalis, a blue precipitate is formed and the liquid acquires the odour of dimethylamine. *Tetramethyldiaminophenotoloxazine*,



prepared by reduction with zinc and hydrochloric acid, is a greyish-white, crystalline powder and is easily reconverted into the dye. *Dimethyldiethyldiaminophenotolazo-oxonium iodide*,  $C_{19}H_{24}ON_3I$ , prepared from 2-dimethylamino-4-hydroxytoluene and nitrosodiethylaniline, crystallises from alcohol in violet-blue crystals; its solution in water, alcohol, or glacial acetic acid has a more reddish-blue colour than that of the tetramethyl derivative. The isomeric *dimethyldiethyldiaminophenotolazo-oxonium iodide*, prepared from 2-diethylamino-4-hydroxytoluene and nitrosodimethylaniline, forms greenish-blue solutions in water, alcohol, acetone, or glacial acetic acid; it is more soluble in water than the preceding compound and its solution in concentrated sulphuric acid is reddish-violet, whilst that of the isomeride is reddish-brown. Capri-blue, G.O.N., is the corresponding zinc chloride double salt.

*Phenyldimethyldiaminophenotolazo-oxonium chloride*,  $C_{21}H_{20}ON_3Cl$ , prepared from dimethylaminocresol and *p*-nitrosodiphenylamine hydrochloride, is a crystalline, indigo-blue powder, soluble in alcohol, acetone, or glacial acetic acid, forming blue solutions, but only very sparingly so in water. Its solution in concentrated sulphuric acid is green, and on dilution becomes violet. as-*Dimethyldiaminophenotolazo-oxonium chloride*,  $C_{15}H_{16}ON_3Cl$ , obtained by the action of dimethylaminocresol on quinonedichlorodi-imide in alcohol at  $40^\circ$ , crystallises with  $1H_2O$ , is readily soluble in water, alcohol, acetone, or glacial acetic acid, and forms a very dark violet solution in concentrated sulphuric acid, which, on dilution, becomes successively red, violet, and blue. Sodium hydroxide precipitates the free base from aqueous solutions of the chloride as a reddish-brown substance which is soluble in ether. as-*Dimethyldiaminotolonaphthazo-oxonium chloride*,  $C_{19}H_{18}ON_3Cl$ , prepared from  $\alpha$ -naphthylamine and nitrosodimethylaminocresol hydrochloride, crystallises from water containing hydrochloric acid in green needles and is readily soluble in water, alcohol, acetone, or pyridine, forming blue solutions tinged slightly with red. Its solution in concentrated sulphuric acid is red, and on dilution becomes yellow. The free base, *dimethylaminotolaminonaphthazo-oxonium hydride*,  $C_{19}H_{17}O_4N_3$ , crystallises from alcohol in orange-red needles. E. W. W.

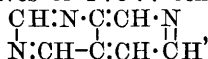
**Antipyrilcarbamide, a Product of the Metabolism of Pyramidone.** By MAX JAFFÉ (*Ber.*, 1902, 35, 2891—2895. Compare Abstr., 1901, i, 672).—From the urine, after administration of pyramidone, antipyrilcarbamide,  $NPh \begin{smallmatrix} CO-C \cdot NH \cdot CO \cdot NH_2 \\ | \\ NMe \cdot CMe \end{smallmatrix}$  (m. p.  $247-248^\circ$ , Knorr, Abstr., 1897, i, 112), has been isolated and identified by conversion into 4-aminoantipyrine; the carbamide gives a violet coloration in aqueous solution with ferric chloride.

K. J. P. O.

**Triethyltrimethylenetriamine.** By ALFRED EINHORN and AUGUST PRETTNER (*Ber.*, 1902, 35, 2942—2944).—Triethyltrimethylenetriamine combines with methyl iodide forming the *methiodide*,  $CH_2 \begin{smallmatrix} NEt \cdot CH_2 \\ | \\ NEt \cdot CH_2 \end{smallmatrix} NEt, MeI$ , which is obtained as a white precipitate melting at  $97-98^\circ$  on adding ethyl acetate to its solution in chloroform. The triamine yields a *hydriodide*,  $C_9H_{22}N_3I$ , which crystallises from alcohol in needles, melts at  $121^\circ$ , and, when treated with alkalis, is reconverted into the base. If this hydriodide is heated for three-quarters of an hour at  $80-90^\circ$ , or if an alcoholic solution of the methiodide is boiled, an isomeric *hydriodide* is obtained; this crystallises in clumps of small needles, melts at  $199^\circ$ , and has the properties of a quaternary ammonium iodide. R. H. P.

**Derivatives of Cinchomeronic Acid.** By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1902, 35, 2831—2852).—The authors have previously (this vol., i, 401) described derivatives of 2:6-benzodi-

azine, for which they proposed the name copyrine. The present paper deals with derivatives of 1:3:7-benzotriazine,



which is named copazoline.

The action of potassium hypobromite on cinchomeronimide is described; the properties of the 3-aminopyridine-4-carboxylic acid obtained differed from those detailed by Blumenfield (Abstr., 1896, i, 60); the melting point varied, according to rate of heating, from 306—310°, the hydrochloride melts and decomposes at 244—245°, and the nitrate at 196—197°. The *methyl* ester crystallises from light petroleum in long, yellowish needles, melts at 86—87°, and forms an *aurichloride* crystallising in yellow needles, and a *platinichloride* forming octahedra-like crystals; its aqueous solution deposits the *hydrate*,  $\text{C}_7\text{H}_8\text{O}_2\text{N}_2 \cdot \text{H}_2\text{O}$ , in long, colourless, silky needles which melt at 50° when quickly heated.

The acid condenses with chloroacetic acid, forming 3-pyridylglycine-4-carboxylic acid,  $\begin{array}{c} \text{N} = \text{CH} \cdot \text{C} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \\ | \quad | \\ \text{CH} \cdot \text{CH} \cdot \text{C} \cdot \text{CO}_2\text{H} \end{array}$ ; this crystallises with

$\text{H}_2\text{O}$  in long needles pointed at both ends, decomposes at about 160°, blackens at 180°, and behaves as a monobasic acid. The *silver* salt,  $\text{C}_8\text{H}_7\text{O}_2\text{N}_2 \cdot \text{Ag} \cdot \text{H}_2\text{O}$ , crystallises in yellowish, pointed needles, and the *barium* salt,  $(\text{C}_8\text{H}_7\text{O}_2\text{N}_2)_2 \cdot \text{Ba} \cdot \text{H}_2\text{O}$ , is a yellow, crystalline powder.

2:4-Dioxycopazoline,  $\begin{array}{c} \text{CO} \cdot \text{NH} \cdot \text{C} \cdot \text{CH} \cdot \text{N} \\ | \quad | \\ \text{NH} \cdot \text{CO} \cdot \text{C} \cdot \text{CH} \cdot \text{CH} \end{array}$ , obtained when 3-aminopyridine-4-carboxylic acid is heated at 170° with carbamide and also when cinchomerondiamide is treated with bromine and sodium hydroxide, is a yellow, microcrystalline powder, sublimes without melting, and is soluble in dilute acids and fixed alkalis. The *hydrochloride* crystallises in small needles and its aqueous solution gives a blue fluorescence when made alkaline with ammonia. The *platinichloride* crystallises in small, short prisms and the *aurichloride* in golden, flat laminae, which sinter at 225° and melt and decompose at 246—248°.

4-Oxycopazoline, prepared from aminopyridinecarboxylic acid and formamide, crystallises from water in clusters of needles, sinters at 300°, and melts and partly sublimes at 315—317°; it dissolves in acids and alkalis; the *potassium* salt forms slender needles, the *platinichloride* yellow needles, the *aurichloride* yellow leaflets, and the *nitrate* colourless leaflets. When shaken with a mixture of phosphorus tri- and penta-chlorides at 160°, it yields 4-chlorocopazoline,  $\begin{array}{c} \text{CH} \cdot \text{N} \cdot \text{C} \cdot \text{CH} \cdot \text{N} \\ | \quad | \\ \text{N} \cdot \text{CCl} \cdot \text{C} \cdot \text{CH} \cdot \text{CH} \end{array}$ , which crystallises from light petroleum in yellowish rods, sinters at 110° and melts at 112°. When the chloro-compound is reduced with a mixture of hydriodic acid and phosphonium iodide at temperatures not exceeding 0°, it yields 3:4- (or possibly 1:2-) *dihydrocopazoline*, which crystallises from acetone or ether, melts at 144—145°, and forms a strongly alkaline aqueous solution; the *hydriodide*,  $\text{C}_7\text{H}_7\text{N}_3 \cdot 2\text{HI}$ , crystallises in yellow, pointed needles which decompose at 260—280°, the *platinichloride*,  $\text{C}_7\text{H}_7\text{N}_3 \cdot \text{H}_2\text{PtCl}_6$ , is an insoluble, orange-yellow, crystalline powder, the *aurichloride*,

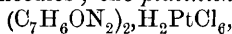
$C_7H_7N_3 \cdot 2HAuCl_4$ , crystallises in golden needles, and the *picrate* and *chromate* are both insoluble.

When condensed with acetamide, the aminopyridinecarboxylic acid yields 4-*oxy*-2-methylcopazoline, which crystallises from water in long, flat needles melting at  $288^\circ$ , can be sublimed, is soluble in acids and alkalis, and forms a crystalline *platinichloride*.

*Cinchmeron 3-amic acid*,  $CO_2H \cdot C_5NH_3 \cdot CO \cdot NH_2$ , obtained when cinchmeronimide is shaken up for 1 hour with a normal solution of potassium hydroxide, separates from water in clear, rhombic crystals, decomposes at  $200^\circ$ , forming the imide, and when treated with bromine and sodium hydroxide yields 3-aminopyridine 4-carboxylic acid; the *silver* salt crystallises in white leaflets.

Cinchmerondiamide is best prepared by digesting the imide with alcoholic ammonia and crystallises in transparent cubes and melts at  $175-176^\circ$ , forming the imide; its aqueous solutions deposit the *hydrate*,  $C_7H_7O_2N_3 \cdot H_2O$ , in glassy prisms, which with silver nitrate form the crystalline additive compound,  $2C_7H_7O_2N_3 \cdot AgNO_3$ .

When cinchmeronimide is reduced with tin and hydrochloric acid, *cinchmeronimidine*,  $\begin{array}{c} N-CH:C-CO \\ | \quad | \\ CH \cdot CH:C \cdot CH_2 \end{array} > NH$ , is obtained; this crystallises with  $H_2O$  in compact, yellow prisms, or from acetone or ethyl acetate in clusters of yellowish needles; the *platinichloride*,



separates in amber-coloured, octahedral crystals, the *aurichloride* in leaflets, and the *picrate* in needles which darken at  $200^\circ$ ; the *hydrochloride*,  $C_7H_6ON_2 \cdot HCl \cdot H_2O$ , crystallises in compact, glassy prisms, which lose their colour at  $225^\circ$  and melt and decompose at  $248-250^\circ$ , and the *stannichloride*,  $C_7H_6ON_2 \cdot HSnCl_3 \cdot H_2O$ , crystallises in compact, pointed rods.

Cinchmeronimidine, when heated at  $180^\circ$  with red phosphorus and hydriodic acid, yields a mixture of 4-methylpyridine-3-carboxylic acid, methyl- and dimethyl-pyridine, and a new di-acid base, *merimine*,  $\begin{array}{c} N-CH:C-CH_2 \\ | \quad | \\ CH \cdot CH:C \cdot CH_2 \end{array} > NH$ .

Merimine is an oil, and in aqueous solution is strongly alkaline and absorbs carbon dioxide; the *hydrochloride* forms colourless, flat crystals, the *platinichloride* a yellowish-red powder consisting of needles, the *aurichloride* compact prisms, and the *picrate* an insoluble, crystalline powder which decomposes at  $211-212^\circ$ .

*isoNitrosocinchmeronimidine* was obtained as a yellow, microcrystalline powder which sublimes when heated and is decomposed by hydrochloric acid, yielding cinchmeronic acid, hydroxylamine, and ammonia. The *platinichloride* is a yellow, crystalline powder, and the *aurichloride* crystallises in small, slender needles. R. H. P.

**Isomerism of antiDiazo hydrates and Primary Nitrosoamines.** By ARTHUR HANTZSCH and WILLIAM POHL (*Ber.*, 1902, 35, 2964—2978).—The authors show that antidiazotates,  $\begin{array}{c} R \cdot N \\ | \\ N \cdot OM \end{array}$ , when treated with carbon dioxide, yield yellow, primary nitrosoamines,

$R \cdot NH \cdot NO$ . The *antidiazohydrates*, which are all white when treated with hydrochloric acid, yield diazonium salts, but the nitrosoamines yield hydrochlorides of the type  $NO \cdot NHR, HCl$ . A further difference is shown by the rate of coupling, as the antidiazohydrates couple much quicker than do the nitrosoamines.

An aqueous solution of 2 : 6-dibromoanisole diazonium nitrate yields, when treated with an ice-cold concentrated solution of potassium hydroxide, *potassium syndiazo-2 : 6-dibromoanisole*,  $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{N} \begin{smallmatrix} \text{N} \\ \text{OK} \end{smallmatrix}$ , which

was obtained as an unstable, white precipitate, and, when treated with a hot concentrated solution of potassium hydroxide, yields the isomeric *potassium antidiazo-2 : 6-dibromoanisole*, which crystallises in stable needles. The *antidiazotate*, when treated with acetic acid, yields the white 2 : 6-dibromoanisole *antidiazohydrate*,  $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{N} \begin{smallmatrix} \text{N} \\ \text{OH} \end{smallmatrix}$ , which

is reconverted into *antidiazotate* when treated with alkalis, and when treated with hydrochloric acid, acetyl chloride, or phosphorus pentachloride yields the diazonium chloride. When the potassium *antidiazotate*, dissolved in ice-cold water, is treated with carbon dioxide, the 2 : 6-dibromoanisole *nitrosoamine*,  $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{NH} \cdot \text{NO}$ , is obtained; this is an amorphous substance of a deep yellow colour, behaves as a pseudo-acid, and when treated with an ethereal solution of hydrogen chloride, forms a *hydrochloride* which crystallises in small, bright yellow needles.

*Benzophenone-p-antidiazohydrate* was obtained as a white, voluminous precipitate, and *benzophenone-p-nitrosoamine* as a yellow, unstable substance.

*Potassium 2 : 4 : 6-tribromobenzeneantidiazotate* crystallises in reddish needles which are very unstable; the corresponding *antidiazohydrate* is obtained when an ice-cold solution of *antidiazotate* is acidified with acetic acid, as a white precipitate, which is immediately transformed to the orange-yellow, amorphous 2 : 4 : 6-tribromophenyl *nitrosoamine*; this is also obtained when the corresponding diazonium salts are treated with a solution of sodium acetate; it melts and decomposes at  $85-86^\circ$  and forms a light yellow *hydrochloride* and *hydrobromide*. The *antidiazotates*, *antidiazohydrates*, and *nitrosoamine*, obtained from 2 : 4 : 6-tribromo-*m*-toluidine, are very similar to the compounds derived from 2 : 4 : 6-tribromoaniline, but are much less stable.

*Potassium 2 : 6-dibromo-p-tolueneantidiazotate* crystallises in long, white needles, the *antidiazohydrate* and the *nitrosoamine* are unstable. The analogous *p*-nitro-, *o*-nitro-, and *p*-bromo-compounds were prepared, and are very similar to the substances just described. R. H. P.

**Diazoisonitrosomethyluracil and 4-Aminopyrazole.** By GEORG WOLLERS and ROBERT BEHREND (*Annalen*, 1902, 323, 279—283).—Diazoisonitrosomethyluracil may be regarded as having either the constitution  $\text{NH} \cdot \text{CO} \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{N} \cdot \text{OH} \\ \text{CO} \cdot \text{NH} \cdot \text{C} \cdot \text{CH} \cdot \text{N} \cdot \text{OH} \end{smallmatrix}$  or  $\text{NH} \cdot \text{CO} \cdot \text{C} \begin{smallmatrix} \text{N}(\text{NO}_2) \\ \text{CO} \cdot \text{NH} \cdot \text{C} \cdot \text{CH}_2 \end{smallmatrix} \gg \text{N}, \text{H}_2\text{O}$ . On reduction, it yields isooxanthine,  $\text{NH} \cdot \text{CO} \cdot \text{C} \begin{smallmatrix} \text{NH} \\ \text{CO} \cdot \text{NH} \cdot \text{C} \cdot \text{CH} \end{smallmatrix} \gg \text{N}$ , and this sub-

stance, when heated with concentrated hydrochloric acid at 150—190°, loses the elements of ammonia and carbon dioxide and becomes converted into 4-aminopyrazole,  $\text{NH}_2\text{C}(\text{CH}=\text{NH})\text{CH}=\text{N}$ , which is characterised by its *nitrate*,  $\text{C}_3\text{H}_5\text{N}_3 \cdot 2\text{HNO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ , and its *benzoyl* derivative,  $\text{C}_3\text{H}_3\text{N}_3\text{Bz}_2$ ; these compounds crystallise in needles, and the latter melts at 173°. G. T. M.

**Syntheses with Hippurazoimide.** By THEODOR CURTIUS (*Ber.*, 1902, 35, 3226—3228).—The following compounds have been prepared by condensing hippurazoimide with glycine,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , or glycylglycine,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .

Benzoylglycylaminoacetic acid yields a *hydrazide* melting at 227—229° and an *azoimide* melting at 109—110°.

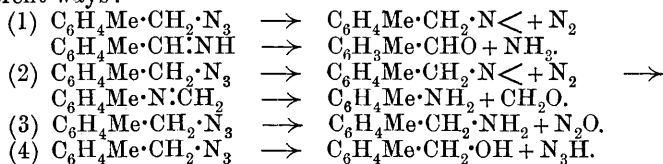
*Benzoylglycylglycylaminoacetic acid*,

$\text{NHBz}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  
melts at 215—216°, its *ethyl* ester at 173°, its *hydrazide* at 245—250°, and its *azoimide* at 162°.

*Benzoylglycylglycylglycylaminoacetic acid*,

$\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  
melts at 235° and its *amide* at 213°. T. M. L.

**4-Methylbenzylazoimide.** By THEODOR CURTIUS and A. DARAPSKY (*Ber.*, 1902, 35, 3229—3233).—*p*-Methylbenzylazoimide is stable towards alkalis, but is readily decomposed by acids in a similar manner to benzylazoimide. The decomposition proceeds in four different ways:



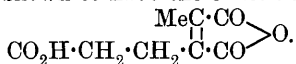
The products actually obtained were hydrazoic acid, *p*-methylbenzyl chloride, *p*-methylbenzaldehyde (converted into the aldazine), ammonia, *p*-toluidine, and *p*-methylbenzylamine. T. M. L.

**Azoaldoximes and Hydrazidines.** By HUGO VOSWINCKEL (*Ber.*, 1902, 35, 3271—3274).—Since the composition of phenylazoacetaldoxime has been settled, the constitution of the following substances previously described by the author can be fixed:  $\text{C}_8\text{H}_8\text{O}_4\text{N}_3\text{Cl}$ , *p*-chlorophenylazoacetaldoxime (*Abstr.*, 1899, i, 958);  $\text{C}_8\text{H}_{10}\text{ON}_3\text{Cl}$ , *p*-chlorophenylhydrazoacetaldoxime (*ibid.*);  $\text{C}_9\text{H}_{11}\text{ON}_3$ , *p*-tolylazoacetaldoxime (*ibid.*);  $\text{C}_9\text{H}_{13}\text{ON}_3$ , *p*-tolylhydrazoacetaldoxime (*ibid.*);  $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_4$ , carbanilphenylazoacetaldoxime (*Abstr.*, 1901, i, 53);  $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}_3$ , acetylphenylazoacetaldoxime (*ibid.*); and  $\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_6$ , picrylphenylazoacetaldoxime (*ibid.*). The oxygen-free reduction products have been proved to be hydrazidines (amidrazones), and the constitutions of the compounds previously described are:  $\text{C}_8\text{H}_{11}\text{N}_3$ , phenylethenylhydrazidine,  $\text{NHPh}\cdot\text{NH}\cdot\text{CMe}\cdot\text{NH}$  (*Abstr.*, 1899, i, 958);  $\text{C}_9\text{H}_{13}\text{N}_3$ ,

phenylmethylethenylhydrazidine (*ibid.*); and  $C_8H_{10}N_3Cl$ , *p*-chloro-phenylethenylhydrazidine.

*Phenylethenylhydrazidine hydrochloride*,  $NHPh \cdot NH \cdot CMe : NH, HCl$  or  $NHPh \cdot N : CMe \cdot NH_2, HCl$ , is obtained by the action of phenylhydrazine on acetimino-ethyl ether in ethereal solution; hydrochloric acid is then added and the ether evaporated. The azidine hydrochloride is separated from the unattacked phenylhydrazine by means of alcohol. It forms silky needles which contain  $\frac{1}{2}H_2O$ . The hydrated salt melts at  $140^\circ$ , then loses water, and resolidifies, after which it melts at  $205^\circ$ . When a mixture in molecular proportion of this salt and hydroxylamine hydrochloride is left in concentrated aqueous solution with double the molecular quantity of potassium carbonate, slender, orange needles of *phenylazoacetaldoxime* separate. Phenylhydrazoacetaldoxime, when boiled with alcohol to which water has been added, gives, after the addition of hydrochloric acid, *ethenyl-phenylhydrazidine hydrochloride*. J. McC.

**Hæmatin.** By WILLIAM KÜSTER (*Ber.*, 1902, 35, 2948—2954. Compare Abstr., 1901, i, 298).—The anhydride,  $C_8H_8O_5$ , previously described (*loc. cit.*) is shown to have the constitution



When oxidised, it yields succinic acid, and when reduced by means of hydrogen iodide, a mixture of two isomeric "*hæmotricarboxylic*" acids having the constitution of pentane- $\alpha\gamma\delta$ -tricarboxylic acids. These were separated by crystallisation from water; the more soluble (1 in 7.3 parts of water at  $10^\circ$ ) melts at  $140$ — $141^\circ$  and the other (1 in 75 parts of water at  $10^\circ$ ) at  $175$ — $176^\circ$ : the isomeride with the lower melting point is converted into the other form by heating either alone or with water or with hydrochloric acid at  $200^\circ$ . The electrical conductivities of both acids are far less than the conductivities of tricarboxylic acids as determined by Zelinsky (*Abstr.*, 1896, i, 349). The isomeride of higher melting point was also obtained from the imide,  $C_8H_9O_4N$ , previously described (*loc. cit.*).

Acetyl hæmin and  $\beta$ -hæmin, when treated with aniline, yield two amorphous products, *hæmeins*, which have the empirical formulæ  $C_{34}H_{32}O_4N_4Fe$  and  $C_{35}H_{34}O_4N_4Fe$  respectively.

Experiments are described which tend to show that the oxidation with chromic acid of the hæmopyrrole described by Nencki and Zaleski (*Abstr.*, 1901, i, 434) yields the anhydride of methyl-*n*-propyl-maleic acid. R. H. P.

**Lacto-serum.** By ERNST FULD (*Beitr. chem. Physiol. Path.*, 1902, 2, 425—429).—Lacto-serum (Bordet) is obtained by immunising animals (rabbits in the present research) with milk; their serum then causes a precipitate when added to milk. The reaction is a precipitation of the caseinogen, but the presence of calcium salts is essential, although they may be replaced imperfectly by barium salts. The other proteids are not involved. If the original immunisation is produced with cow's milk, it is only cow's milk or its caseinogen which gives the reaction; goat's milk is easily precipitable with

rennet, but not by this lacto-serum; human caseinogen gives scarcely any reaction. A given quantity of lacto-serum can only precipitate a certain quantity of caseinogen. The product has not the same insolubility in salt solution that casein has. Digestion of lacto-serum with a third of its volume of horse-serum has no influence.

W. D. H.

**Specific Precipitins.** By PHILLIPPE EISENBERG (*Bull. Acad. Sci. Cracow*, 1902, 289—310).—The experiments were performed by immunising rabbits against egg-albumin and horse-serum. A suggestion for quantitative work on the 'precipitins' obtained is to take measured quantities of the serum diluted so that it only just gives the reaction. The amount of precipitin 'absorbed' means that which takes part in the process of precipitation. The 'precipitin' has many of the characters of coagulated albumin and contains both precipitin and 'precipitable substance,' but not all of either. An excess of both is present which can be detected by a further precipitate occurring when more of either substance is added. Excess of 'precipitable substance' inhibits precipitation; this is attributed to an inhibitory substance in the 'precipitin.' All immune substances are not contained in the pseudo-globulin fraction, but were found also in the eu-globulin fraction of the serum.

W. D. H.

**Action of Superheated Steam on Keratin.** By RICHARD BAUER (*Zeit. physiol. Chem.*, 1902, 35, 343—357. Compare Krukenberg, *Sitzungsber. Jena Ges. Naturwiss.*, 1886).—When keratin, obtained from horn shavings, is heated with water in sealed tubes at 150° for 24 hours, considerable amounts of hydrogen sulphide and a second volatile sulphur compound, presumably methyl mercaptan, are formed. The solution contains two compounds corresponding with Neumeister's atmidalbumin and atmidalbumose, which the author terms *atmidkeratin* and *atmidkeratose*. They are most readily obtained by concentrating the solution and saturating it with powdered sodium chloride when atmidkeratin is precipitated. The filtrate from this precipitate, on treatment with hydrochloric acid saturated with sodium chloride, yields first a mixture of the two compounds and then atmidkeratose.

The compounds are only slowly acted on by pepsin and trypsin.

J. J. S.

**Glutineptone.** By W. FAHRION (*Chem. Zeit.*, 1902, 26, 675—677).—Glutineptone, obtained by warming animal hide or gelatin with alcoholic sodium hydroxide, is strongly basic. Unlike its hydrochloride, it is insoluble in alcohol. The saponification number increases with the duration of warming with alkali; the increase is more rapid in aqueous solution than in aqueous-alcoholic solution. The saponification number is lower when air is completely excluded than when it has free access to the solution. From this behaviour, it is concluded that glutineptone contains no alcoholic hydroxyl groups, and that it is not an aldehyde, ketone, or lactone. A determination of the equivalent of uric acid showed that it increases in the same way as that of glutineptone; from this, it is assumed that the high value of



the saponification number of glutinpeptone on prolonged heating is due to the presence of imino-groups united to carbonyl groups.

When glutinpeptone is oxidised in alkaline solution with potassium permanganate, a substance is obtained which is insoluble in alcohol, but which gives a soluble hydrochloride; at the same time, butyric acid is formed, and a very small quantity of benzoic acid.

Glutinpeptone scarcely absorbs iodine, indicating that it does not contain doubly-linked carbon atoms in an open chain. J. McC.

**Nucleic Acid from Embryos of Wheat.** By THOMAS B. OSBORNE and ISAAC F. HARRIS (*Zeit. physiol. Chem.*, 1902, **36**, 85—133. Compare Abstr., 1900, i, 573).—The embryos of wheat contain relatively large amounts of a nucleic acid which the authors term *triticonucleic acid*. Some 3.5 per cent. of the acid is contained in the commercial flour freshly obtained from wheat embryos, but the amount rapidly diminishes when the flour is kept. The acid has most of the properties characteristic of the nucleic acids of animal origin, but is much less readily soluble in water. Its percentage composition agrees best with the formula  $C_{41}H_{61}O_{31}N_{16}P_4$ . It forms *acid potassium*, *sodium*, and *ammonium* salts, which are soluble in water, yielding solutions with strongly alkaline properties, and it is found to be practically impossible to obtain the acid free from mineral matter.

When hydrolysed with mineral acids, triticonucleic acid yields guanine (1 mol.), adenine (1 mol.), uracil (2 mols.), and pentoses (3 mols.).

The *silver* salt contains six atoms of silver, and the free acid presumably contains six hydroxyl groups. It is suggested that the acid is formed by the condensation of four  $P(OH)_5$  groups, the four atoms of phosphorus being united with the aid of three oxygen atoms. When boiled for a short time with dilute acids, only one-fourth of the total phosphorus is obtained in the form of orthophosphoric acid, and a complex phosphorus acid is produced by the elimination of one atom of phosphorus together with guanine, adenine, and a molecule of pentose.

Triticonucleic acid may be identical with the nucleic acid obtained from yeast and somewhat resembles guanylic acid. J. J. S.

**alloOxyproteic Acid, a Normal Constituent of Urine.** By STANISLAUS BONDZYŃSKI and K. PANEK (*Ber.*, 1902, **35**, 2959—2963).—Analyses are given of the *barium* and *silver* salts of a new acid, *allooxyproteic acid*, which the authors have isolated from urine. The acid contains carbon, hydrogen, oxygen, nitrogen, and sulphur, appears to be a normal constituent of urine, and is very similar to oxyproteic acid (Abstr., 1898, i, 501); it does not give the typical reactions of proteids, and has not yet been isolated in the pure state.

R. H. P.

**Isolation of Malt Enzymes and the Proteolytic Enzyme of Malt.** By CARL J. LINTNER (*Chem. Centr.*, 1902, ii, 288—289; from *Zeit. ges. Brauw.*, **25**, 365—368).—The malt enzymes are best isolated

by salting out with ammonium sulphate. The small precipitate first obtained on addition of the sulphate has a distinct diastatic, but scarcely any proteolytic, action; the active enzyme is precipitated on further addition of the sulphate. The enzymes isolated by this means are capable of liquefying gelatin and have a diastatic action or fermentative power of 143, whilst that of the enzyme obtained by precipitation with alcohol seldom rises above 80. The experiments confirm the presence of a proteolytic enzyme in malt, but do not indicate that it plays any important part in the mashing process. The assumption that it resembles trypsin and determines the decomposition of proteids during germination is unfounded. When liquefied gelatin is digested with the enzymes for 48 hours at 40°, the gluten is scarcely attacked, and only a very slight peptonisation could be detected by means of the biuret reaction. The fermentative action of the enzymes should rather be compared with that of malt extracts which have been attenuated by heating and which, although capable of liquefying starch paste, are unable to convert the starch into sugar.

E. W. W.

**Yeast-gum and Invertase.** By KINTARO OSHIMA (*Zeit. physiol. Chem.*, 1902, 36, 42—48. Compare Salkowski, Abstr., 1894, i, 221, 316; 1895, i, 166; 1901, i, 180).—When yeast gum is distilled with hydrochloric acid of sp. gr. 1.060, the distillate gives the reaction for methylfurfuraldehyde (Abstr., 1901, ii, 484) and the original gum presumably contains a methylpentosan. When the gum is hydrolysed with sulphuric acid, the chief product is *d*-mannose.

Attempts were made to purify crude invertase (Osborne, Abstr., 1899, i, 967). If the extraction with chloroform at 34° is continued for several days, the yield of invertase is somewhat better, but the product contains larger amounts of gum.

A considerable amount of the gum is thrown down in the first fraction when the clear chloroform extract is fractionally precipitated with 93 per cent. alcohol. A simpler method for the removal of gum is to precipitate the invertase from a neutral solution of Osborne's crude product with a 5 per cent. solution of copper acetate, to wash thoroughly, precipitate the copper as sulphide, and to pour the filtrate, freed from hydrogen sulphide, into alcohol. J. J. S.

**Invertase of Yeast. Quantitative Experiments on the Action of Alcohol and Acids on this Enzyme.** By THOMAS BOKORNY (*Chem. Zeit.*, 1902, 26, 701—703. Compare Abstr., 1901, ii, 568).—The author's experiments demonstrate that the inverting action of yeast is not effected by the living protoplasm, but by a material which can be separated from the yeast cell: this view was originally expressed by Berthelot in 1860. Four grams of fresh yeast extract at 45—50° in 15 minutes can convert from 68 to 82 per cent. of a sucrose solution varying in strength from 5 to 20 per cent. Dried yeast has in no way lost this power. When kept for several days under absolute alcohol at the ordinary temperature, the inverting action of yeast is unimpaired, but at 45° it is completely destroyed. Similarly, 5 per cent. formaldehyde has little effect at the

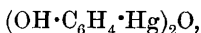
ordinary temperature, but destroys the inverting power at 45°. Dried yeast extract is changed but little as regards inverting power by keeping in 0.5 per cent. oxalic acid, 0.5 per cent. hydrofluoric acid, 2 per cent. acetic acid, or 2 per cent. lactic acid.

K. J. P. O.

[Formation of Aromatic Mercury Compounds.] By LEONE PESCI (*Zeit. anorg. Chem.*, 1902, 32, 227—234. Compare Abstr., 1898, i, 648; 1901, i, 576).—A claim for priority against Dimroth (this vol., i, 656). The author also defends the views he has expressed previously on the constitution of the compounds obtained from aniline and mercuric acetate and other mercury aromatic compounds against Dimroth's criticisms.

J. McC.

[Formation of Aromatic Mercury Compounds.] By OTTO DIMROTH [and, in part, RICHARD METZGER] (*Ber.*, 1902, 35, 2853—2873. Compare Abstr., 1899, i, 154, 428, and this vol., i, 656).—The hydroxyphenylmercury salts (previously described) dissolve in dilute sodium hydroxide; carbon dioxide precipitates from the solution of the ortho-compound the internal anhydride of *o*-hydroxyphenylmercury hydroxide,  $C_6H_4 \begin{smallmatrix} Hg \\ \diagup \diagdown \\ O \end{smallmatrix}$ ; from the para-compound, an oxide,

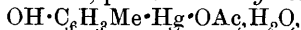


is obtained as an insoluble, white powder which cannot be converted into *o*-phenylenemercury oxide.

The pharmaceutical preparation, *Hydrargyrum carbolicum*, which is prepared by heating sodium phenoxide and mercuric chloride in alcoholic solution, and is generally considered to be a mercury phenoxide, is now shown to consist mainly of a mixture of *o*- and *p*-hydroxyphenylmercury oxides and hydroxyphenylenedimercury oxide.

*o*-Mercuryphenol,  $(OH \cdot C_6H_4)_2Hg$ , is prepared by treating *o*-hydroxyphenylmercuric chloride with sodium thiosulphate; it crystallises in lustrous, white plates, which become coloured on heating and dissolve in alkali hydroxides, but not in carbonates. The hydroxyphenylmercury salts give, with nitrous acid, at first coloured solutions and then coloured precipitates which resemble those obtained by the action of Millon's reagent on phenols, proteids, &c.

*p*-Cresol and mercuric acetate, in mol. proportion, give equal quantities of a mono- and a di-mercury compound; at 100°, only the di-mercury compound is formed; *p*-cresolmercury acetate,



is obtained by crystallising the product of the reaction from acetic acid; it decomposes at 200°; addition of sodium chloride to the mother liquor precipitates *p*-cresolmercury chloride,  $OH \cdot C_6H_3Me \cdot HgCl$ , which crystallises in needles melting at 166° and decomposing at 176°, when it becomes solid. The corresponding iodide is prepared from the chloride and potassium iodide, and crystallises in slender needles which begin to decompose at 145°; the acetate, prepared by dissolving the oxide in acetic acid, crystallises in leaflets melting and decomposing at 163°. The oxide,  $C_6H_3Me \begin{smallmatrix} Hg \\ \diagup \diagdown \\ O \end{smallmatrix}$ , is prepared as a white powder by dissolving

the chloride in dilute sodium hydroxide and then precipitating with carbon dioxide; the *sodium* salt,  $\text{ONa} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{Hg} \cdot \text{OH}$ , crystallises in very soluble needles. The *benzoyl* derivative,  $\text{OBz} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{HgCl}$ , prepared by the Schotten-Baumann method, crystallises in slender needles melting at  $241-242^\circ$ .

*o-Iodo-p-cresol*,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{MeI}$ , is prepared by the action of iodine on the iodide previously mentioned; it crystallises in hair-like needles melting at  $35^\circ$  and boiling at  $117^\circ$  under 12 mm. pressure.

Benzenediazonium chloride reacts with *o*-phenylmercury chloride, forming the *azo*-compound,  $\text{N}_2\text{Ph} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{HgCl}$ , which is a reddish-brown powder melting at  $147^\circ$ ; it forms a stable *additive* product with 1 mol. of acetic acid, which crystallises in yellowish-brown needles melting at  $126-128^\circ$ ; a hydrate with 1 or  $1\frac{1}{2}\text{H}_2\text{O}$ , is obtained when water is added to the alcoholic solution and crystallises in slender, yellow needles, which lose water when dried over sulphuric acid, forming a very hygroscopic, red powder; when dried at  $100^\circ$ , a red powder is obtained which is no longer hygroscopic. The *azo*-compound just mentioned combines with acids; the *compound* with hydrogen chloride is a red powder melting at  $160^\circ$ . When the *azo*-compound is boiled with hydrochloric acid, it is converted into *p*-hydroxyazobenzene. *p*-Hydroxyphenylmercury chloride and benzenediazonium chloride yield mainly *p*-hydroxyazobenzene together with a small quantity of a *substance*, probably benzeneazo-*p*-hydroxyphenylmercury chloride; the latter melts at  $130-131^\circ$ , and forms a crystalline *additive* product with one mol. of acetic acid. Hydroxyphenyldimercury acetate and the diazonium chloride give chiefly *benzeneazo-o-hydroxyphenylmercury acetate*; it crystallises in yellow prisms melting at  $197-198^\circ$ ; *benzeneazohydroxyphenyldimercury chloride*, as an *additive* product with 1 mol. of acetic acid, was also isolated by precipitating with sodium chloride and crystallising the product from acetic acid; it melts and decomposes at  $165-170^\circ$ . *Benzeneazo-p-cresolmercury acetate*,  $\text{N}_2\text{Ph} \cdot \text{C}_6\text{H}_2\text{Me}(\text{OH}) \cdot \text{Hg} \cdot \text{OAc}$ , forms red needles melting and decomposing at  $269^\circ$ ; the *chloride*, prepared from the acetate, crystallises in yellowish-brown, silky needles melting and decomposing at  $249^\circ$ ; both these compounds are soluble with difficulty in alkalis.

*Thymolmercury chloride*,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{MePr} \cdot \text{HgCl}$ , is prepared by adding sodium chloride to the acetic acid solution of the product of the reaction of mercuric acetate and thymol; it crystallises in needles melting at  $139.5^\circ$ ; the *sodium* salt forms needles; *thymoldimercury acetate*,  $\text{OH} \cdot \text{C}_6\text{HMePr}(\text{Hg} \cdot \text{OAc})_2$ , separates directly from the product of the reaction of thymol and mercuric acetate, and forms needles melting and decomposing at  $215-216^\circ$ ; the *sodium* salt crystallises in leaflets.

A mixture of resorcinolmercury chloride and resorcinoldimercury chloride is obtained by adding sodium chloride to the product of the interaction of mercuric acetate and resorcinol; chloroform extracts the *monomercury* compound,  $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{HgCl}$ , which crystallises in prisms containing chloroform and melts at  $105^\circ$ ; when free from chloroform, it melts at  $123^\circ$ ; it is decomposed by water, and yields a solution in sodium hydroxide, rapidly becoming coloured. *Resorcinoldimercury chloride* forms an insoluble, white powder which begins to

decompose at 200°. Quinol does not form a mercury compound, but is oxidised to quinhydrone by mercuric acetate.

Phenol ethers, such as anisole, and phenetole, react with mercuric acetate less readily than the phenols, and yield substances which have previously been described.

*o*-Benzophenonemercury chloride,  $\text{COPh} \cdot \text{C}_6\text{H}_4 \cdot \text{HgCl}$ , is prepared by heating together dry mercuric acetate and excess of benzophenone, converting the acetate thus formed into chloride by means of sodium chloride, and separating the insoluble dimercury compound by ether; the monomercury compound, crystallises in leaflets melting at 167—168°; the *dimercury* compound is a yellowish powder. *o*-Benzophenonemercury bromide melts at 176°, and is converted by bromine into *o*-bromobenzophenone (m. p. 35°). Acetophenone and mercuric acetate yield *phenacylmercury chloride*,  $\text{COPh} \cdot \text{CH}_2 \cdot \text{HgCl}$ , the nucleus not being attacked; this substance forms needles melting at 145—146°, and is easily decomposed by bromine, giving phenacyl bromide.

Anhydrous mercuric benzoate is obtained from the hydrated salt by crystallisation from chloroform; it forms crystals melting at 165°; when heated at 170°, it is converted into a compound,  $\text{C}_6\text{H}_5 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{Hg} \end{smallmatrix} \text{O}$ , which forms a powder soluble in alkali hydroxides and carbonates, and is changed by sodium chloride into *chloromercuribenzoic acid*; when treated with bromine, *o*-bromobenzoic acid is formed.

When dry mercuric salicylate is heated at 100°, it is converted into salicylic acid and a compound,  $\text{OH} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{Hg} \end{smallmatrix} \text{O}$ , which is the anhydride of *o*-hydroxymercurisalicylic acid; it is a white powder, soluble in alkalis, and identical with the pharmaceutical preparation, *Hydrargyrum salicylicum*. By iodine, it is converted into *o*-iodosalicylic acid, consequently the mercury is attached to the benzene nucleus in the ortho-position relatively to the hydroxyl group.

K. J. P. O.

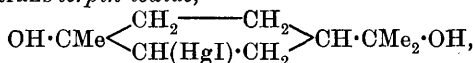
**Mercuric Compounds from Terpeneol and Dimethylheptenol.** By JULIUS SAND and FRITZ SINGER (*Ber.*, 1902, 35, 3170—3187).—Characteristic products cannot be obtained by shaking ethereal terpeneol with aqueous mercuric nitrate or sulphate; crystalline products can, however, be obtained by dissolving yellow mercuric oxide in 20 per cent. nitric acid, adding potassium hydroxide until basic nitrate begins to separate, and shaking with ethereal terpeneol solution, the alkali and terpeneol being added alternately until mercurous oxide begins to be precipitated; the solution is made strongly alkaline, and on addition of potassium iodide gives an immediate precipitate of mercuricineol iodide, a gradual separation of  $\alpha$ -mercuric *trans*-terpin iodide from the filtrate, and a further separation of  $\beta$ -mercuri-*trans*-terpin iodide on passing carbon dioxide into the solution.

*Mercuricineol iodide*,  $\text{CMe} \begin{smallmatrix} \text{CH}_2 - \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CMe}_2 \\ \diagdown \quad \diagup \\ \text{CH}(\text{HgI}) \cdot \text{CH}_2 \end{smallmatrix} \text{CH}$ , crystallises from

alcohol in small, glistening prisms, dissolves very readily in cold benzene or chloroform, becomes yellow at 115°, and melts and decom-

poses at 152—154°. The *chloride* crystallises from alcohol in white, felted needles, melts constantly and sharply at 162°, and, unlike the iodide, is readily soluble in alkali. The iodide does not yield a benzoate, and when reduced with sodium amalgam does not yield a terpineol, but a mobile oil, which gives precipitates with hydrogen chloride, bromide, and ferrocyanide, and is therefore in all probability cineol.

*α-Mercuri-trans-terpin iodide*,

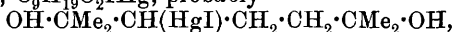


separates from benzene in glistening, colourless prisms, is sensitive to light, becomes red at 120°, and melts and decomposes at 144°. It combines with alcohol to form the *alcoholate*,  $\text{C}_{10}\text{H}_{19}\text{O}_2\text{IHg} \cdot \text{C}_2\text{H}_6\text{O}$ , which crystallises from alcohol in glistening needles, and becomes red and melts at 123—125°. The iodide is reduced by sodium amalgam, or by electrolysis at a platinum cathode, to *trans-terpin* (m. p. 156°).

*β-Mercuri-trans-terpin iodide* melts at 38°, separates from organic solvents as an oil, and, like the preceding compound, is reduced by sodium amalgam to *trans-terpin*; when boiled with organic solvents, it is readily converted into the stable *α*-compound. The *α*- and *β*-compounds are probably stereoisomerides, differing only in the position of the  $\text{-HgI}$  group; as the *α*-compound is readily reconverted into terpineol by mineral acids, it probably has the  $\text{-HgI}$  group in the *cis*-position relatively to the adjacent hydroxyl, whilst the *β*-compound, which is only slowly decomposed, would have the  $\text{-HgI}$  in the *trans*-position.

*Dimethylheptenol*,  $\text{CMe}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{OH}$ , prepared by Grignard's method from methylheptenone and magnesium methiodide, is a highly refractive oil, and boils at 85—86° under 14 mm. pressure (uncorr.). Towards mercury salts, it behaves in just the same way as terpineol, giving an *iodide*,  $\text{C}_9\text{H}_{17}\text{OIHg}$ , which is insoluble in alkalis,

and probably has the structure,  $\text{CMe}_2 \begin{array}{c} \text{CH}(\text{HgI}) \cdot \text{CH}_2 \\ \text{O} \text{---} \text{CMe}_2 \end{array} > \text{CH}_2$ , together with an *iodide*,  $\text{C}_9\text{H}_{19}\text{O}_2\text{IHg}$ , probably



soluble in alkalis, which separates from benzene in glistening crystals, becomes yellow and melts at 124—125°, and probably also an isomeric oily iodide,  $\text{C}_9\text{H}_{19}\text{O}_2\text{IHg}$ .

T. M. L.

# JOURNAL

OF

## THE CHEMICAL SOCIETY.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

PART II.

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### General and Physical Chemistry.

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**Secondary Reactions in Grove's Gas Battery.** By EUGEN VON BIRON (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 474—480).—The author has measured the potential, relatively to that of a normal calomel electrode, of a platinised platinum electrode saturated with air in hydrochloric acid of different concentrations, the method of measurement being compensation by means of a capillary electrometer. The following table contains the mean values obtained, the concentrations being given in multiples of the normal strength :

Concentration.....	4	2	1	0.4	0.2	0.1	0.04	0.01
Potential	0.733	0.723	0.718	0.707	0.690	0.685	0.670	0.634

These results are compared with those given by Smale (Abstr., 1894, ii, 436) for an oxygen electrode in sulphuric and hydrochloric acids of the same concentrations as the above. In the case of sulphuric acid, the oxygen electrode gives slightly greater potentials than those of the author, but the numbers decrease with the concentration in a similar way. The values obtained by Smale for an oxygen electrode in hydrochloric acid show, however, a decided increase (from 0.415 to 0.665) as the concentration of the acid diminishes from 5 to 0.1 normal whilst with further dilution the potential decreases to 0.583 for 0.00025 *N* acid; this behaviour he explained as due to the action of chlorine ions formed by oxidation of the strong hydrochloric acid by

the oxygen. This explanation the author considers erroneous, as his own values show no such behaviour.

T. H. P.

**Cathodic Polarisation and Formation of Alloys.** By ALFRED COEHN (*Zeit. physikal. Chem.*, 1901, 38, 609—629).—The discharge potential of metallic ions at the cathode diminishes as a current is passed through an electrolyte solution and this is due to the formation of an alloy of the discharged metal and the metal of the cathode. This was ascertained by measuring the polarisation of the cathode against a normal (gas) electrode. The phenomenon is most clearly exhibited by a mercury cathode, but solid metals also form alloys. The cathodes used were mercury, platinum, copper, silver, and gold, and solutions of zinc, cadmium, iron, copper, silver, and mercury salts were examined.

The investigation of solutions containing ionic hydrogen leads to the conclusion that only with palladium is an alloy formed, since only with that metal as electrode could the discharge potential be lowered below the point of reversible separation of bubbles of gas. The curve representing the depression of the discharge potential, with *E.M.F.* applied with solutions of potassium hydroxide, shows two breaks. The first corresponds with the formation of a potassium alloy with the electrode; the second with the formation of a potassium hydrogen ion which cannot alloy with the electrode (mercury), but is decomposed by it. By applying the law of mass action, it is deduced that this substance has the formula  $KH_2$ .

When ammonium salts are used, the same phenomenon is observed as when alkali salts are examined, and this is evidence that ammonium amalgam exists and that ammonium is of a metallic nature.

J. McC.

**Dielectric Constants of Pure Solvents.** By HERMAN SCHLUNDT (*J. Physical Chem.*, 1901, 5, 503—526).—In continuation of previous work (*Abstr.*, 1901, ii, 299), the dielectric constants of a large number of organic and inorganic compounds have been determined, among them many amines and nitro-compounds. The following are the values of the dielectric constant for some of the more important compounds:—Ethylene cyanide, 61.2 at 60°; ethylamine, 6.17 at 21°; nitromethane, 40.4 at 19°; nitroethane, 29.5 at 18°; methyl nitrate, 23.5 at 18°; ethyl nitrate, 18.3 at 18°; phosphorus trichloride, 3.36 at 22°; arsenic trichloride, 12.35 at 21°; antimony trichloride, 33.2 at 75° (liquid); 5.4 at 18° (solid); stannic chloride, 3.2 at 22°; phosphorus oxychloride, 13.9 at 22°; sulphuryl chloride, 9.15 at 22°; liquid sulphur dioxide, 12.35 at 22° (compare Coolidge, *Abstr.*, 1900, ii, 4); bromine, 3.18 at 23°; liquid cyanogen, 2.52 at 23°. In homologous series, the dielectric constant diminishes as the molecular weight increases. The introduction of the cyanogen group in a compound causes a large increase in the value of the dielectric constant. There is no anomalous absorption in compounds containing a cyanogen, an amino-, or a nitro-group. Whilst a number of cases have been discovered where the Nernst-Thomson rule is applicable, striking exceptions to that rule have also been found, showing that the nature of the solvent is of prime importance in determining whether a solution



will conduct electricity. Obach's law is found to hold only approximately for the nitriles.

J. C. P.

**Electrical Conductivity of Sodium and Potassium Hydroxides in Glycerol.** By GIUSEPPE DI CIOMMO (*Il Nuovo Cimento*, 1901, [v], 2, 81—87).—The author has measured the electrical conductivities of solutions of various concentrations and at various temperatures, of sodium and potassium hydroxides in 96 per cent. glycerol, the method of measurement being that of Kohlrausch. The results, which are given in the form both of tables and curves, show that the conductivities are much less than those of aqueous solutions of the hydroxides, the maximum values in glycerol being less than one-millionth of those in water. At the temperatures employed, 14° to 30°, the maximum conductivity of sodium hydroxide in glycerol occurs with a concentration of 5 per cent., the corresponding concentration for potassium hydroxide being 7.03 per cent. These concentrations are directly proportional to the molecular weights of the two hydroxides, a relation which does not hold in the case of aqueous solutions. The temperature coefficients of the conductivities are very high, reaching the values 0.21 and 0.17 for sodium and potassium hydroxides, whilst for aqueous solutions the maximum values of these coefficients are 0.03 and 0.07 respectively. In both glycerol and water, the maxima of conductivity correspond with weaker solutions of sodium than of potassium hydroxide.

T. H. P.

**Dispersion of the Lines of Current in Electrolytes.** By W. PFANHAUSER, jun. (*Zeit. Elektrochem.*, 1901, 7, 895—897).—In electroplating objects of irregular shape, the author considers that the current lines tend to concentrate at the points of the cathode nearest to the anode, just as the lines of force in the magnetic field of a horse-shoe magnet are most concentrated at the points of the poles which are nearest together. The lines of current are more evenly spread over the whole surface of the object with some electrolytes than with others, and the author proposes the theory that the spreading is proportional to the difference between the discharge potentials of the cations of the "conducting salt" (usually  $K^+$ ,  $Na^+$ , or  $H^+$ ) and of the metal which is to be deposited.

T. E.

**Dissociation Relationships of Ternary Electrolytes.** By KARL DRUCKER (*Zeit. physikal. Chem.*, 1901, 38, 602—608).—Assuming that a ternary electrolyte,  $AB_2$ , can only dissociate into  $A^+$ ,  $AB^+$ , and  $B'$  (or  $A''$ ,  $AB'$ , and  $B^+$ ), then  $(G' - G) = (c - e)$ , where  $G'$  is the osmotic concentration (obtained from a cryoscopic determination),  $G$  the concentration determined analytically,  $c$  the concentration of the ions  $B'$ , and  $e$  the concentration of the undissociated substance. If  $e$  is very small, then  $(G' - G) = c$ . The results of Loomis (*Abstr.*, 1896, ii, 352; 1897, ii, 305) and Wildermann (*Abstr.*, 1896, ii, 351) on the freezing point of solutions of sulphuric acid give values for  $(G' - G) = c$  (the concentration of hydrogen ions), which agree with the values calculated for  $c$  from the conductivity of sulphuric acid solutions (up to 0.1*N*), assuming that  $c_{H_2SO_4} = 0$ . The author concludes that in 0.1*N* sulphuric

acid solution, although the degree of dissociation is only 0.55, no  $\text{HSO}_4'$  is present. J. McC.

**Influence of Electrical Waves on Chemical Action.** By FELIX LENGFELD and JAMES H. RANSOM (*J. Physical Chem.*, 1901, 5, 502).—Electrical waves of 300 metres are without effect on mixtures of hydrogen and chlorine or hydrogen and oxygen. J. C. P.

**Phenomenon observed in the Inversion of Flame.** By E. MANELI and M. COMELLA (*Gazzetta*, 1901, 31, ii, 255).—A modification of the lecture experiment, showing, by the burning of air in coal gas, that the terms combustible and supporter of combustion are merely relative, is described, by which it is possible to produce an isolated flame which does not appear at the orifice of either the gas or air tube; the flame obtained consists of two parts, in one of which the gas burns in air, whilst in the other the air burns in the coal gas. T. H. P.

**Determination of the Calorific Power of Fuels.** By UBALDO ANTONY and E. DI NOLA (*Gazzetta*, 1901, 31, ii, 277—284).—A reply to the criticisms of Rebuffat (*Abstr.*, 1901, ii, 373) on the authors' previous paper (*Abstr.*, 1901, ii, 6) on Berthier's method of determining the calorific value of fuels. T. H. P.

**Heat developed by the Action of Oxygen on Alkaline Pyrogallol.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1901, 133, 664—666).—The action of oxygen on a solution of pyrogallol in potassium hydroxide develops, at first, 60 Cal. for each atom of oxygen absorbed, but the quantity of heat liberated for a given quantity of oxygen absorbed becomes less as the action proceeds. The development of heat is progressive, even at first, and seems to be due to several consecutive reactions. C. H. B.

**Inversion Points of Heats of Dilution.** By ALBERT COLSON (*Compt. rend.*, 1901, 133, 585—587).—If curves are constructed representing the heat of dissolution against temperature for solutions of sodium chloride at different concentrations, it is found that they cut at the temperature  $52^\circ$ . This is, hence, an inversion point for the heat of dilution, which becomes zero. Addition of hydrogen chloride or sodium hydroxide causes a rise of this temperature of inversion, the values  $80^\circ$  and  $83^\circ$  being obtained in  $N$  solutions of these compounds, and  $100^\circ$  and  $100.8^\circ$  in  $2N$  solutions. L. M. J.

**Thermodynamics of Concentrated Solutions.** By A. SCHÜKAREFF (*Zeit. physikal. Chem.*, 1901, 38, 543—560).—In a system consisting of two components, it is deduced that  $\mu - \mu_0 = k'(1/c_0 - 1/c)$  and  $\mu' - \mu'_0 = k'(1/c'_0 - 1/c')$ , where  $\mu$  is the potential when the concentration is  $c$ . This is the same as Gibbs' formula, provided that  $c$  and  $c'_0$  do not lie far apart. It is the expression for the work done on introducing each unit of substance into the system, provided that no chemical action takes place. The author applies this to (a) the distribution of a substance between two immiscible solvents, or between a

liquid and a solid solvent, (b) speed of solution, (c) diffusion (in solution), and (d) depression of solubility by addition of a salt containing the same cation.

J. McC.

**New Proof of the Formula  $d = 0.02T^2/L$ .** By FELIX LENGFELD (*J. Physical Chem.*, 1901, 5, 499—501).—The proof is based on the supposition that the solvent may be supercooled indefinitely, and that the specific heats of the solid and liquid are constants from absolute zero to the normal melting point.

J. C. P.

**Pipette for Determining the Density of Liquids.** By FERNAND GIRARDET (*Bull. Soc. Chim.*, 1901, [iii], 25, 936—943).—The apparatus, of which a figure is given in the paper, consists of two vertical glass tubes the lower ends of which dip respectively into water and the liquid under examination, whilst the upper extremities are connected with a rubber tube by which suction may be applied. Behind each tube is a paper scale. The heights to which the two liquids rise are inversely proportional to their densities. The paper gives details of the construction and use of the instrument, and also a mathematical demonstration of its principle, sensibility, and relative error.

N. L.

**Laws of Internal Friction.** By LADISLAUS NATANSON (*Zeit. physikal. Chem.*, 1901, 38, 690—704).—A mathematical paper in which the laws of internal friction of liquids are deduced from the consideration of the inequalities of pressure produced in a liquid during a deformation.

L. M. J.

**Viscosity of Helium and its Alteration with Temperature.** By H. SCHULTZE (*Ann. Phys.*, 1901, [iv], 6, 302—314).—By a method previously used in the case of argon (*Ann. Phys.*, 1901, [iv], 5, 140), the author finds the viscosity of helium at 15° to be 1.086 times as great as that of air, whereas Rayleigh found the ratio to be 0.96. For  $n$  and  $c$  (compare Rayleigh, *Abstr.*, 1900, ii, 590; 1901, ii, 9), the author's values agree well with those obtained by Rayleigh.

L. C. P.

**Plastic and Adhesive Properties of Glass at the Ordinary Temperature.** By JULES PICCARD (*Ber.*, 1901, 34, 3635—3639).—A regular even scratch was made with a diamond on a glass plate which was then broken into some twelve rectangular strips. One-half of the strips were clamped at one end in a horizontal position with the scratch on the upper surface, and weights were placed on the free ends until the plate snapped along the scratch. The remainder of the plates were clamped as before but with the scratch on the under surface and the free ends weighted with small weights varying from 50—375 grams, and were left in this position for several days at the ordinary temperature. When the plates were reversed and weights placed on the free ends until the plates broke, it was found that in all these cases the weights required were some 20 per cent. greater than

in the first series of plates. This would indicate that the scratch, which was originally 0.1 mm. in depth, had been partially healed owing to the plastic and adhesive properties of the glass under slight pressure. J. J. S.

**Determination of the Molecular Weights of Volatile Substances by the Boiling Point Method. Behaviour of Iodine and some Inorganic Oxyhaloids.** By GIUSEPPE ODDO (*Gazzetta*, 1901, 31, ii, 222—243. Compare Oddo and Serra, Abstr., 1900, ii, 73 and 74).—The molecular weight of a volatile compound, as determined by the boiling point method, is given by the formula:  $M = (c_2 - c_1)K/\Delta$ , where  $c_2$  and  $c_1$  are the concentrations of the dissolved substance in the solution and in the vapour respectively,  $K$  the molecular increase of boiling point of the solvent and  $\Delta$  the observed rise in boiling point; or, representing  $c_1/c_2$ , which is almost constant for different concentrations, by  $\alpha$ ,  $M = c_2(1 - \alpha)K/\Delta$ . The author has devised an apparatus which is a modification of Beckmann's and allows the necessary data for the above calculation to be obtained from one experiment. It consists of a glass adapter for holding the thermometer, ground to fit the boiling tube; the thermometer may be either ground in or fixed by means of a thin ring of cork. The side tube of the flask is connected in a similar manner with a condenser which can be used either for reflux or, by rotation in the side tube, for distillation. The apparatus is used as follows: The boiling tube having been charged with the solvent and surrounded by a vapour jacket, the boiling point of the solvent is measured in the ordinary way; the substance is then added and the boiling point of the solution measured. The heating is then suspended for a few moments while the condenser is turned into the position for distillation and connected with a tared flask which is surrounded with ice. After a certain quantity of liquid has been distilled over, the temperature is again read and the flasked re-weighed. The amount of dissolved substance in the distillate is then determined. The compounds examined by this method were: (1) iodine in chloroform, tetrachloromethane, ethyl alcohol, and benzene; (2) phosphorus oxychloride in tetrachloromethane, benzene, and chloroform; (3) thionyl chloride in chloroform; (4) phosphorus oxybromide in benzene; (5) phosphorus sulphochloride in benzene; (6) sulphur monochloride in tetrachloromethane and benzene. From these results, which are given in detail, and those previously obtained (*loc. cit.*), the author draws the following conclusions: in boiling carbon disulphide, benzene, or alcohol, the molecule of iodine is diatomic, whilst in chloroform and tetrachloromethane tetratomic molecules are also found. The colour of iodine solutions is not influenced by the number of atoms in the molecule, since carbon disulphide, chloroform, and tetrachloromethane all yield violet solutions. Some of the inorganic oxyhaloid compounds also tend to polymerise in certain solvents; this is principally the case with phosphorus oxychloride in tetrachloromethane in which the mol. weight is 194—250, and in benzene in which the values vary from 228 to 234, the simple molecule having a weight of 153.5; polymerisation also occurs, although to a less degree, with thionyl chloride in

chloroform, phosphorus oxybromide and sulphochloride in benzene, and to a very slight extent with sulphur monochloride in tetrachloromethane and benzene. In freezing benzene, all these oxyhaloids exist in a non-polymerised condition, as also do chromyl and sulphuryl chlorides. Phosphorus oxydichloromonoanilide,  $\text{NHPh} \cdot \text{POCl}_2$ , shows a marked tendency to polymerise in both freezing and boiling benzene. The phenoxy-derivatives of phosphorus oxychloride,  $\text{PhO} \cdot \text{POCl}_2$  and  $\text{PO}(\text{OPh})_3$ , exist as simple molecules in boiling benzene. Phosphorus pentachloride is not polymerised in boiling tetrachloromethane, but sulphur has the formula  $\text{S}_8$ ; the mono- and tri-chlorides of iodine lower the boiling point of this solvent, owing to dissociation.

T. H. P.

**Solubility of Salts. IX. Barium Oxalate.** By E. GROSCHUFF (*Ber.*, 1901, 34, 3313—3325).—The *hydrate*,  $\text{BaC}_2\text{O}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ , is obtained by mixing at  $0^\circ$  concentrated solutions of ammonium oxalate and barium chloride, and is also frequently formed in place of the dihydrate on mixing at  $0^\circ$  dilute solutions of barium hydroxide and oxalic acid; it forms minute, white, pointed needles, is stable at  $18^\circ$ , but effloresces to the hemihydrate in warm weather, and is also converted to the same hydrate by shaking with water. It dissolves in 215 mols. of water at  $0^\circ$ , 152 mols. at  $9.5^\circ$ , 111 mols. at  $18^\circ$ , and 73.4 mols. at  $30^\circ$ .

The *hydrate*,  $\text{BaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , is best prepared by the slow decomposition of the acid oxalates by water at the atmospheric temperature; it is also formed when oxalic acid is neutralised with barium hydroxide or barium carbonate. It forms hexagonal, monoclinic tablets, and is the easiest of all the hydrates to recognise under the microscope. Above  $50^\circ$ , it decomposes to the hemihydrate. It dissolves in 236 mols. of water at  $0^\circ$ , 103 mols. at  $30^\circ$ , 50 mols. at  $65^\circ$ , and 43.8 mols. at  $73^\circ$ .

The hydrate,  $\text{BaC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , is formed above  $50^\circ$ , and best at  $100^\circ$ , on extracting the acid oxalate with water, on heating the anhydrous salt or any of the other hydrates with water, or on heating any of the dry hydrates; it also appears frequently at  $0^\circ$  in place of the hydrate with  $3\frac{1}{2}\text{H}_2\text{O}$ . It forms obliquely truncated, four-sided prisms, and is soluble in 144 mols. of water at  $0^\circ$ , in 76.2 mols. at  $50^\circ$ , and in 59.2 mols. at  $100^\circ$ .

The anhydrous salt crystallises in forms similar to those of the hemihydrate; it is formed by heating the hemihydrate at  $140$ — $150^\circ$ , and is readily reconverted into it by boiling water.

The hydrate,  $\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ , described by several authors, does not appear to exist.

The solubility curves for  $\text{BaC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , and  $\text{BaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , intersect at  $40^\circ$ ; above this temperature, the hemihydrate is the less soluble, and would be the form stable in contact with water, whilst below  $40^\circ$  the dihydrate is the stable and less soluble form. The curve for the hydrate with  $3\frac{1}{2}\text{H}_2\text{O}$  does not intersect that for the dihydrate above  $0^\circ$ , but the curves, if produced, would intersect at a point corresponding with a temperature slightly below  $0^\circ$ ; the hydrate with  $3\frac{1}{2}\text{H}_2\text{O}$  must therefore always be a labile form when in contact with water.

The values given for the solubility are much lower than those previously observed; this is probably due to supersaturation.

The *acid oxalate*,  $\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , undergoes a reversible decomposition in presence of water, and in contact with the solid salt its solutions contain oxalic acid and barium oxalate and are saturated both with regard to the neutral and the acid oxalate. At  $0^\circ$ , 100 mols. of water dissolve from the acid oxalate 0.054 mol.  $\text{H}_2\text{C}_2\text{O}_4$  and 0.0024 mols.  $\text{BaC}_2\text{O}_4$ , or 22 mols.  $\text{H}_2\text{C}_2\text{O}_4$  to 1 mol.  $\text{BaC}_2\text{O}_4$ ; at  $99^\circ$ , 100 mols. dissolve 2.39 mols.  $\text{H}_2\text{C}_2\text{O}_4$  and 0.141 mol.  $\text{BaC}_2\text{O}_4$ , the ratio being 17 to 1. The temperature at which oxalic acid and barium oxalate would dissolve in mol. proportions, that is, at which the acid salt would dissolve without decomposition, lies far below the temperature of experiment; the temperature at which the acid salt would be completely decomposed and the solution become saturated with regard to both barium oxalate and to oxalic acid also lies beyond the temperature of experiment; the salt is therefore within its "transition limits" (Meyerhoffer, *Zeit. physikal. Chem.*, 1890, 5, 120) throughout the whole range of observation. T. M. L.

**State of Dissolved Compounds deduced from Partition Coefficients.** By ARTHUR HANTZSCH and AUGUST VAGT (*Zeit. physikal. Chem.*, 1901, 38, 705—742).—If a compound is divided between two mutually insoluble liquids, then the ratio of the concentrations should be independent of the quantity dissolved, that is, the partition coefficient should be constant. If dissociation occurs in one solvent, then the equilibrium must only be considered for the undissociated molecules, that is  $C_1(1-x)/C_2 = \text{constant}$ . It has been shown, however, by Hantzsch and Sebaldt (*Abstr.*, 1900, ii, 69) that the partition coefficient in the case of amines varies greatly with temperature changes. This work has been considerably extended, and the influence of temperature on a large number of partition coefficients has been determined. The partition coefficients were found to be independent of temperature in the following systems—mercuric chloride in water and toluene, hydrogen cyanide in water and benzene, ethylene cyanide in water and chloroform, acetone in water and toluene, formaldehyde in water and ether, chloral hydrate in water and ether or toluene. For these, therefore, the partition laws hold, and the solvents may be regarded as indifferent, that is, having no effect on the molecular state of the solute. This was not the case, however, in the following cases—trimethylamine, triethylamine, pyridine, or collidine in water and toluene; here the coefficient decreased with rise of temperature, whilst as a similar decrease was obtained when the toluene is replaced by ether, the cause must be sought in the aqueous solution, and the authors consider it is due to the formation of hydrates which decompose with rise of temperature. Similar results were obtained for the systems bromine in water and air, and iodine in glycerol (or aqueous glycerol) and chloroform, so that halogen hydrates or glycerates are indicated. A constant coefficient is obtained, however, for iodine in glycerol and ether, so that iodine etherates also exist. It is noteworthy that when two iodine solutions are of similar colour they yield a constant partition coefficient. Temperature changes caused varia-

tions in the opposite sense with solutions of ferric or chromium thiocyanates in water and ether, the relative concentration of the aqueous solution increasing with temperature. The authors hence consider that ethereal compounds decomposed at higher temperatures must be formed. For compounds of the type of amines also the coefficient increases on dilution. The effect of added compounds was also partially investigated, but the completion and consideration of this work is postponed.

L. M. J.

**Simultaneous Equilibrium and the Relations between Thermodynamics and Velocity of Reaction of Homogeneous Systems.** By RUDOLF WEGSCHEIDER (*Monatsh.*, 1901, 22, 849—906. Compare Euler, *Abstr.*, 1901, ii, 57).—By purely mathematical treatment, the relations between the conditions of equilibrium found by a thermodynamical method and those obtained from a kinetic standpoint are considered. The author comes to the conclusion that different conditions of equilibrium result from each method of treatment, and discusses the meaning of this paradox.

K. J. P. O.

**Limit of Chemical Reactions and of the Product  $PV$ .** By A. PONSOT (*Compt. rend.*, 1901, 133, 618).—The author states the following conclusions.

a. The two hypotheses: (1) that  $PV$  tends to a limiting value for  $V = \infty$ , (2) that chemical reactions may be complete, are incompatible.

b. The two hypotheses: (1) that  $PV$  tends to a limiting value for  $V = \infty$ , (2) that chemical reactions are always limited, are compatible.

c. The two hypotheses: (1) that  $P = 0$  for very great values of  $V$ , (2) that there are complete and limited chemical reactions, are compatible.

L. M. J.

**Velocity of Reaction of Bromine on Ethyl Alcohol.** By STEFAN BUGARSZKY (*Zeit. physikal. Chem.*, 1901, 38, 561—601).—Bromine reacts on an aqueous solution of ethyl alcohol in the cold at a measurable rate; the speed is not constant throughout the reaction, for, as the concentration of hydrogen bromide increases, more bromine is withdrawn from the sphere of reaction by formation of hydrogen tribromide ( $\text{HBr}_3$ ) and so the reaction slackens. Provided that the alcohol is in excess and that the action takes place in the cold, no bromine substitution products are formed, and the only other product of the reaction besides hydrogen bromide is ethyl acetate.

No constant could be obtained for the expression of a reaction of the first, second, or third order from the results obtained at  $25^\circ$  for the extent of reaction after the lapse of known times with solutions of bromine (up to 0.008 gram-molecule per litre) in alcohol to which  $1/5$  of its volume of water had been added. The application of the formulae of Ostwald and of Noyes for the determination of the order of a reaction in which secondary changes take place leads to the conclusion that the action of ethyl alcohol on bromine is unimolecular. Van't Hoff's formula also shows that the reaction is unimolecular, and, since the value obtained with the aid of the latter formula is more nearly  $= 1$  than that obtained with the former, it is clear that the disturbance is

caused by a product of the reaction. It has been proved experimentally that the hydrogen bromide, and not the ethyl acetate, is the disturbing factor. The first reaction,  $2\text{C}_2\text{H}_5\text{O} + 2\text{Br}_2 \rightarrow \text{C}_4\text{H}_8\text{O}_2 + 4\text{HBr}$ , is unimolecular, and the second reaction,  $\text{HBr} + \text{Br}_2 \rightleftharpoons \text{HBr}_3$ , takes place at an incomparably greater rate. It is deduced that the velocity of the primary reaction is given by  $k = 1/(t - t_0) \cdot \log(T_0/T)$ , where  $T_0$  is the concentration of bromine at time  $t_0$ , and  $T$  that at time  $t$ . The value of  $K$ , the equilibrium constant of the secondary reaction, is found from the expression  $K = 1/(t - t_0) \cdot \Sigma/k \cdot \log(T_0/T)$ , wherein  $\Sigma$  is the sum of the concentrations of bromine and hydrogen bromide. The mean value obtained for  $k$  from five series of measurements is 0.1052. The value obtained for  $K$  is 0.00441. Addition of lithium or ammonium bromide in 0.1*N* solution does not alter the value of  $k$  and this is in consonance with the electrolytic dissociation of  $\text{HBr}_3$  into  $\text{H}^+$  and  $\text{Br}_3^-$ . The values of  $k$  obtained from solutions containing bromine in greater concentration than 0.01*N* are not constant, but if mercuric bromide be added to the solution, then the bromine ions which are formed are taken up with production of  $\text{HgBr}_4$  (Abstr., 1893, ii, 566) and the reaction proceeds unimolecularly.

J. McC.

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## Inorganic Chemistry.

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**Reactions of Hydrogen Peroxide.** By ARNOLD NABL (*Monatsh.*, 1901, 22, 737—744. Compare Abstr., 1901, ii, 16, 94).—Hydrogen peroxide and sodium thiosulphate react according to the equation:  $2\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}_2 = 2\text{NaOH} + 2\text{Na}_2\text{S}_4\text{O}_6$ . If the alkali is not neutralised, 75 per cent. of the thiosulphate remains unoxidised and the reaction leads to the formation of sulphate and dithionate as well as tetrathionate:  $2\text{Na}_2\text{S}_2\text{O}_3 + 7\text{H}_2\text{O}_2 = 2\text{Na}_2\text{SO}_4 + \text{H}_2\text{S}_2\text{O}_6 + 6\text{H}_2\text{O}$ ;  $\text{H}_2\text{S}_2\text{O}_6 + \text{H}_2\text{O}_2 = 2\text{H}_2\text{SO}_4$ .

Barium sulphite and hydrogen peroxide give a small quantity of dithionate as well as of sulphate when the sulphite is in excess. The reactions represented by the equations  $2\text{H}_2\text{SO}_3 + \text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{H}_2\text{S}_2\text{O}_6$  and  $\text{H}_2\text{S}_2\text{O}_6 + \text{H}_2\text{O}_2 = 2\text{H}_2\text{SO}_4$ , therefore take place simultaneously.

K. J. P. O.

**Alkali Salts of Hydrogen Peroxide in Aqueous Solution.** By HARRY T. CALVERT (*Zeit. physikal. Chem.*, 1901, 38, 513—542).—An historical account of the peroxides of the alkali metals is given. For the experiments, the hydrogen peroxide was prepared by repeated distillation until the conductivity was constant, and then concentrated on the water-bath. The distribution ratio of hydrogen peroxide between water and ether at 20° is 15·6 and is independent of the concentration. A constant ratio (7·03 at 25°, and 6·65 at 0°) was also found when the ether was replaced by amyl alcohol, and this is not altered by the addition of acids. In presence of alkalis, the distribu-

tion ratio is increased and the curve representing the change of ratio with increasing concentration of hydrogen peroxide approaches asymptotically to a line denoting the ratio on the assumption that 1 mol. of alkali fixes  $1\frac{1}{2}$  mols. of hydrogen peroxide. Addition of hydrogen peroxide diminishes the saponifying power of sodium hydroxide, indicating that hydroxyl ions disappear.

The conductivity of hydrogen peroxide solutions was determined in a modified Kohlrausch cell, in which the electrodes consisted of tinned iron, which does not catalyse the solution. The conductivity of alkali salt solutions is very slightly diminished by addition of hydrogen peroxide; that of solutions of hydroxides of the alkali metals is very greatly reduced. This is explained on the assumption that with the hydroxyl ions the hydrogen peroxide forms superoxide ions, the migration-velocity of which is small compared with that of the hydroxyl ions. Using the Ostwald-Walden rule, the author calculates the migration-velocity of this new anion to be 48.5 (Kohlrausch and Holborn units), the same value being found from solutions containing the cations  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$ .

The migration of the superoxide anion has been proved experimentally by the method described by Noyes and Blanchard (Abstr., 1901, ii, 91), lead oxide being used as indicator.

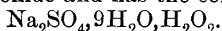
From the depression of the freezing point of water containing sodium hydroxide and hydrogen peroxide, using excess of the latter to diminish the hydrolysis, it is shown that the anion is univalent and is derived from the hydroxyl ion and neutral hydrogen peroxide (Abegg and Bodländer, Abstr., 1899, ii, 542). The results are in agreement with the assumption that the ion is  $\text{O}'_2$  and the compound formed from sodium hydroxide and hydrogen peroxide is  $\text{NaO}'_2$ .

The solubility of potassium chlorate in hydrogen peroxide is much greater than that in pure water, and consequently such a determination could not be used to ascertain if the hydrogen peroxide forms a complex ion with the cation.

J. McC.

**Molecular Compounds of Hydrogen Peroxide with Salts.** By SIMEON L. TANATAR (*Zeit. anorg. Chem.*, 1901, 28, 255—257).—The compound  $\text{KF}\cdot\text{H}_2\text{O}_2$  is obtained by dissolving potassium fluoride in 15 per cent. hydrogen peroxide and evaporating at  $50^\circ$  so long as no serious decomposition occurs. It crystallises in monoclinic needles, is not hygroscopic, but exceedingly soluble in water, is not decomposed at  $70^\circ$  and only partially so at  $110^\circ$ , and is fairly stable when dry.

A similar compound is obtained by dissolving sodium sulphate in 3 per cent. hydrogen peroxide and has the composition



With sodium nitrate, the double salt,  $\text{NaNO}_3\cdot\text{Na}_2\text{O}_2\cdot 8\text{H}_2\text{O}$ , is obtained. It is very unstable.

E. C. R.

**Generalisations on Halogen Double Salts.** By HORACE L. WELLS (*Amer. Chem. J.*, 1901, 26, 389—408).—A long list is given of halogen double salts of the alkali metals, ammonium, and univalent thallium, with negative metals; the salts are arranged according to types, which are designated by ratios indicating the number of atoms of each metal present.

The remarkable similarity in the prominent types of the series of different valencies leads to the conclusion that the valency of the metal of a negative haloid has no influence on the types of double salts which it forms. The molecules of alkali haloids have nearly the same combining power as molecules of negative haloids. Salts of simple types (particularly the 2:1 and 1:1 ratios) predominate. Remsen's law which states that the number of alkali haloid molecules which can combine with a negative haloid molecule is not greater than the valency of the metal of the latter, must be abandoned. The double haloids appear to increase in variety and ease of formation from the iodides to the fluorides. They may be classified in three groups, based upon their behaviour in solution. (1) Salts, such as potassium platinichloride, which undergo ionisation into alkali metal ions and complex negative ions. (2) Salts which readily separate into their component haloids in solution, but can be recrystallised unchanged from water or from dilute acid solutions. (3) Salts which require the presence of an excess of one of their component haloids in solution for their formation.

E. G.

**Tri-iodides.** By YUKICHI OSAKA (*Zeit. physikal. Chem.*, 1901, **38**, 743—749).—The addition of iodine to a solution of potassium iodide or hydrogen iodide produces a rise of the freezing point proportional to the quantity of iodine added, and greater for the hydrogen than for the potassium salt. Hence it follows that the total concentration of ions and undissociated molecules is decreased by the addition of iodine. This necessitates a greater affinity constant for the iodides than for the tri-iodides, so that Dawson's assumption that these affinity constants are equal is incorrect (*Trans.*, 1901, **79**, 238).

L. M. J.

**Influence of the Concentration of the Hydrogen Ions on the Action of Iodates on Haloid Salts.** By HUGO DIRTZ and B. M. MARGOSCHES (*Zeit. angew. Chem.*, 1901, **14**, 1082—1091).—Potassium iodate and iodide readily react in the presence of a small amount of an acid (hydrogen ions) liberating iodine, and the amount thus deposited is directly proportional to the amount of acid present (Fessel, *Zeit. anorg. Chem.*, 1900, **23**, 66). Potassium bromide and iodate do not react so readily in the presence of an acid (Bugarszky, *Abstr.*, 1896, ii, 216) and the iodine ions are only transformed into free iodine when the concentration of the hydrogen ions exceeds a certain minimum. Potassium chloride reacts less readily than the bromide and the necessary concentration of hydrogen ions is much greater.

When definite amounts of hydrochloric or sulphuric acid are added to a potassium iodide solution mixed with an excess of iodate, the amounts of iodine liberated and of iodate left are found to correspond with the amounts required for the given quantities of acid employed. The free iodine was extracted with toluene and titrated with *N*/10 thiosulphate and the residual iodate was titrated by means of the same reagent. When acetic acid is added to a potassium iodide-iodate mixture, the reaction is not normal and the residual iodate is always less than that required by theory; similar results

have been obtained when acetic acid was used in presence of sodium acetate. The anomaly is probably due to the formation of an organic iodine derivative.

Boric acid is not capable of liberating iodine from an iodide-iodate mixture except in the presence of glycerol or dextrose. The same acid does not liberate free halogen from a bromide-iodate mixture, even in the presence of glycerol. Phenol also is incapable of liberating iodine, but picric acid liberates a small amount from an iodide-iodate mixture.

With mixtures of bromide, iodide, and iodate in the presence of acetic or hydrochloric acid, the amount of iodine liberated corresponds with the reaction between the iodide and iodate. A bromate-iodide mixture also yields iodine on treatment with acids, but requires the addition of several c.c. of  $N/10$  acid before the liberation of iodide is started.

A bromide-bromate mixture in the presence of acetic acid and sodium acetate yields no free halogen.

A chlorate-iodide solution, even in the presence of considerable excess of dilute hydrochloric acid liberates but little iodine; concentrated acid, on the contrary, liberates a much larger amount.

J. J. S.

**Supposed Anomalous Behaviour of Oxygen at Low Pressure.** By MAX THIESEN (*Ann. Phys.*, 1901, [iv], 6, 280—301).—The author's observations are quite unfavourable to the supposed existence of an anomaly for oxygen under 0.7 mm. pressure (compare Bohr, *Ann. Phys. Chem.*, 1886, [ii], 27, 459; Rayleigh, *Abstr.*, 1901, ii, 542).

J. C. P.

**Dissociating Power of Hydrogen Sulphide.** By WM. T. SKILLING (*Amer. Chem. J.*, 1901, 26, 383—384).—When a solution of potassium chloride in liquid hydrogen sulphide is placed in a tube provided with platinum electrodes and connected with a battery of 40 volts, no conduction takes place.

E. G.

**Catalytic Reactions. II. Decomposition of Chlorosulphonic Acid into Sulphuryl Chloride and Sulphuric Acid.** By OTTO RUFF (*Ber.*, 1901, 34, 3509—3515).—At  $170^{\circ}$ , the reaction,  $2\text{SO}_3\text{HCl} \rightleftharpoons \text{SO}_2\text{Cl}_2 + \text{H}_2\text{SO}_4$ , is a reversible one, and after 72 hours, the equilibrium reached is  $1\text{SO}_2\text{Cl}_2 : 1\text{H}_2\text{SO}_4 : 2.5\text{SO}_3\text{HCl}$ ; sulphur dioxide and chlorine are not formed between  $170^{\circ}$  and  $190^{\circ}$ , although at a higher temperature they begin to be noticeable. Obviously, therefore, the sulphuryl chloride is not formed by the union of sulphur dioxide and chlorine, initially produced by complete dissociation of the chlorosulphonic acid (compare Heumann and Köchlin, *Abstr.*, 1883, 781), but is a direct decomposition product; this is emphasised by the fact that, when the formation of the sulphuryl chloride occurs at the boiling point of the chlorosulphonic acid owing to the presence of a catalytic agent its amount is not increased by the passage of a current of chlorine and sulphur dioxide through the liquid. When sulphur dioxide and chlorine are produced at a high temperature, they

are due to the latter causing decomposition in the sense of the equation  $\text{SO}_3 + 2\text{HCl} = \text{SO}_2 + \text{H}_2\text{O} + \text{Cl}_2$ .

Mercuric salts rapidly decompose chlorosulphonic acid at its boiling point into sulphuryl chloride and sulphuric acid, and several other salts effect a similar result, only more slowly. The figures after the names of the following salts indicate the number of grams of sulphuryl chloride formed by boiling 50 grams of the acid for 60 minutes with 1 gram of the salt. Mercuric chloride and sulphate, each 13.0; mercury, 12; antimony penta- and tri-chloride, 7.5; stannic chloride, 5.8; bismuth chloride, 3.3; platonic chloride, 2.5; uranyl chloride, 1.7; gold chloride, 1.2; copper sulphate, 0.8; tungsten chloride, 0.8; lead chloride, 0.7; cobalt sulphate, 0.5, and magnesium chloride, 0.5; the chlorides of zinc, aluminium, iron, calcium, and sodium are without action. As the whole of the chlorosulphonic acid is easily decomposed by boiling with mercuric chloride, the method is probably capable of commercial application for the manufacture of sulphuryl chloride.

The mercuric chloride is not changed at all in the action, but mercuric sulphate is converted into mercuric chloride; sodium chloride dissolves in chlorosulphonic acid with evolution of hydrogen chloride and production of the *sodium* salt,  $\text{ONa}\cdot\text{SO}_2\cdot\text{Cl}$ , which is precipitated by the addition of sulphuryl chloride and is readily decomposed by water.

W. A. D.

**Formation of Dithionic Acid.** By JULIUS MEYER (*Ber.*, 1901, 34, 3606—3610).—The formation of barium dithionate, by passing sulphur dioxide into water in which manganese dioxide is suspended, is probably to be represented by the following equations:  $2\text{MnO}_2 + 3\text{H}_2\text{SO}_3 = \text{Mn}_2(\text{SO}_3)_3 + 3\text{H}_2\text{O} + \text{O} = \text{MnS}_2\text{O}_6 + \text{MnSO}_3 + 3\text{H}_2\text{O} + \text{O}$ , as manganese sulphite and sulphate are always formed in appreciable quantity. Ferric hydroxide and sulphurous acid, in the absence of air and at low temperatures, yield ferrous sulphite and ferrous dithionate,  $[\text{Fe}_2(\text{SO}_3)_3] = \text{FeSO}_3 + \text{FeS}_2\text{O}_6$ . Cobaltic and nickelic hydroxides react with sulphurous acid in a similar manner. Lead, barium, magnesium, and sodium peroxides do not yield dithionates on treatment with sulphurous acid (compare Carpenter, *Trans.*, 1902, 81, 1).

The electrical conductivities and freezing points of barium dithionate solutions are given, and the formula  $\text{H}_2\text{S}_2\text{O}_6$  for the acid is considered to be proved (compare Ostwald, *Zeit. physikal. Chem.*, 1887, 1, 106).

J. J. S.

**So-called Sulphimide.** By ARTHUR HANTZSCH and A. HOLL (*Ber.*, 1901, 34, 3430—3445. Compare W. Traube, *Abstr.*, 1892, 1389; 1893, ii, 268).—Sulphamide is unimolecular, and, in the pure state, not an electrolyte, and corresponds with carbamide; sulphimide, on the other hand, is termolecular and corresponds with cyanuric acid. Sulphamide is best purified by repeated crystallisation from ethyl alcohol; it forms rhombic plates melting at  $91.5^\circ$  (Traube,  $75-81^\circ$ ), is perfectly tasteless, and quite neutral. In the preparation of sulphamide by the action of sulphuryl chloride on a light petroleum solution of ammonia, several bye-products are formed, but the composition of these has not been determined.

Trisulphimide,  $\text{OH}\cdot\text{SO}\langle\begin{smallmatrix} \text{N}\cdot\text{SO}(\text{OH}) \\ \text{N}\cdot\text{SO}(\text{OH}) \end{smallmatrix}\rangle\text{N}$ , is crystalline, but the yield is extremely small, and the analytical results do not agree with those required for the pure compound; it may be, however, that it contains combined water. It crystallises from methyl alcohol in colourless, glistening needles, melts at about  $161^\circ$ , is odourless, but has a sharp, acid taste, dissolves in alcohol, and also sparingly in ether, but is insoluble in benzene or chloroform. Aqueous solutions are fairly stable, except when warmed. Ebullioscopic determinations of the molecular weight in ethyl acetate solution point to the formula  $(\text{SO}_2\cdot\text{NH})_3$ . The values obtained for the molecular conductivities of trisulphimide and its salts in aqueous solution show (1) that trisulphimide behaves as a strong acid; (2) that it is tribasic. Further, the conductivity of the potassium salt is nearly the same as that of potassium ferricyanide. The molecular conductivity of silver trisulphimide is much lower than that of potassium trisulphimide at the same dilution.

*Pyridine silver trisulphimide*,  $(\text{SO}_2\text{N})_3\text{Ag}_3\cdot 6\text{C}_5\text{NH}_5$ , crystallises in prisms and is gradually decomposed at  $140^\circ$ . The *N-methyl* derivative,  $\text{SO}_2\langle\begin{smallmatrix} \text{NMe}\cdot\text{SO}_2 \\ \text{NMe}\cdot\text{SO}_2 \end{smallmatrix}\rangle\text{NMe}$ , obtained from the silver salt, forms colourless crystals melting at  $121^\circ$  and readily soluble in most organic solvents. It is not hydrolysed by alkalis and only very slowly by acids, yielding methylamine and sulphuric acid. *Tribenzoylsulphimide*,  $(\text{SO}_2\text{N}\cdot\text{COPh})_3$ , crystallises in prisms melting at  $112^\circ$ . J. J. S.

**Isomorphism of Selenates and Tellurates.** By JAMES F. NORRIS and WILLIAM A. KINGMAN (*Amer. Chem. J.*, 1901, 28, 318—324).—The authors have attempted to prepare isomorphous selenates and tellurates, but without success. All the tellurates except those of the alkali metals are insoluble and the soluble tellurates do not resemble the corresponding selenates in crystalline form, solubility, or amount of water of crystallisation.

*Rubidium hydrogen tellurate*,  $\text{RbHTeO}_4\cdot\frac{1}{2}\text{H}_2\text{O}$ , is a crystalline salt, soluble in about 20 parts of cold water, and slightly more so in hot water. The *cæsium* salt,  $\text{CsHTeO}_4\cdot\frac{1}{2}\text{H}_2\text{O}$ , forms small, cubic crystals and is soluble in about 30 parts of cold water.

*Rubidium hydrogen selenate*,  $\text{RbHSeO}_4$ , is a hygroscopic, well crystallised salt, which dissolves in about its own weight of water. The *cæsium* salt,  $\text{CsHSeO}_4$ , crystallises in large, flat plates with pointed ends and is extremely hygroscopic.

*Rubidium tellurate*,  $\text{Rb}_2\text{TeO}_4\cdot 3\text{H}_2\text{O}$ , crystallises in prisms with pyramidal ends and is soluble in about 10 parts of water. E. G.

**Aqueous Ammonia Solutions.** By FRANZ GOLDSCHMIDT (*Zeit. anorg. Chem.*, 1901, 28, 97—139).—The partial pressure and the conductivity of ammonia solutions (0.5*N*, 0.75*N*, and 1*N*) were determined and the same constants for solutions to which carbamide (1*N* and 1.5*N*) had been added. The vapour tension was measured by the method previously used by Gaus (*Abstr.*, 1901, ii, 7). The increase of the partial pressure of the ammonia is almost exactly proportional to the amount of carbamide added. The values of *k* found from the expression

$(k + \text{H}_2\text{O})/(k + \text{H}_2\text{O}') = \lambda^2 p' / \lambda'^2 p$  is negative and almost exactly constant;  $k$  is the hydration constant,  $\text{H}_2\text{O}$  the active mass of the water (taken as 100),  $\text{H}_2\text{O}'$  the active mass after the addition of the carbamide,  $\lambda$  and  $\lambda'$  are the conductivities, and  $p$  and  $p'$  the ammonia partial pressures of the solutions with and without the carbamide. The variation of the active mass of the water is taken as proportional to the variation of the vapour pressure, on the assumption that only a monohydroxide is formed. No significance can be attributed to the fact that the value of  $k$  is negative.

From the conductivity of ammonia solutions (which show a maximum molecular conductivity), it is found that the dissociation constant ( $K$ ) varies from  $22.1 \times 10^{-6}$  to  $0.23 \times 10^{-6}$  for solutions which are 0.0109  $N$  to 12.89  $N$ . As the solution becomes dilute, the value of  $K$  approaches a constant, and assuming that this begins at the concentration 0.02  $N$ , the value of  $K$  is  $19.1 \times 10^{-6}$ . The inconstancy of the values of  $K$  cannot be attributed to the formation of complex ions such as  $\text{NH}_4 \cdot \text{NH}_3$ , for the lowering of the freezing point of water containing ammonia and ammonium salts corresponds with the value calculated for the quantity of material added.

The addition of ammonia diminishes the conductivity of aqueous salt solutions. The diminution is directly proportional to the quantity of ammonia added and amounts to 2 to 3 per cent. of the value of the conductivity per gram-mol. of ammonia per litre. Lithium salts are most affected in this way by ammonia, sodium salts less so, and potassium salts least. The action of ammonia is independent of the nature of the anion present. It is concluded that the speed of migration of the ions is reduced by the presence of ammonia, and this is also proved thermodynamically.

The influence of ammonia on the conductivity of ammonium chloride, mono-, di-, and tri-methylamine hydrochloride and piperidine hydrochloride is of the same nature as, but much smaller than, that on the alkali salts; with tetramethylammonium chloride, the effect is of the same magnitude as with potassium nitrate.

J. McC.

**Chemical Equilibrium in the Reduction of Nitric Acid by means of Nitric Oxide.** By A. V. SAPOSCHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 506—516. Compare Abstr., 1900, ii, 722).—The author's previous experiments (*loc. cit.*) on the decomposition of nitrous acid according to the equation,  $3\text{HNO}_2 = \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O}$ , having failed to yield the equilibrium constant of the reaction, he has now studied the inverse change, the method of experiment being to pass nitric oxide through nitric acid of a certain strength and to determine from time to time the electrical conductivity of the solution. At the end of each experiment, the amount of nitrous and nitric acids and of nitric oxide in the liquid was determined. On calculating the constants of equilibrium for acids of varying concentration from the formula,  $K = c^3/x^2c_1^2$ , where  $c$  and  $c_1$  are the concentrations of the nitrous and nitric acids respectively in the final solution, and  $x$  the degree of dissociation of the nitric acid, it is found that for nitric acids of  $N$  to  $N/10$  initial concentration, the constant ( $\times 10,000$ ) varies within the limits 142 and 178 and has a mean value of 159; for

acid of 0.05*N* concentration, the constant is 232, the high value being probably due to the fact that at such great dilution the reaction proceeds very slowly and possibly does not reach its final point; with acids of higher concentration than normal, the constant falls regularly, a behaviour probably explained by the final product of the reaction consisting partly of oxides of nitrogen mixed with the nitrous acid. The coefficient of absorption of nitric oxide in litres of gas per litre of acid is given for each different nitric acid employed; Kahlbaum's acid, having a sp. gr. 1.517 at 15°/4°, contains 0.88 per cent. of nitric oxide, the coefficient of absorption in this case being 12.5. The speed of the absorption of nitric oxide by nitric acid varies to a very large extent with the concentration of the acid, as is shown by curves connecting litres of the gas absorbed with time in hours. T. H. P.

**Allotropy of Phosphorus.** By RUDOLF WEGSCHEIDER and FELIX KAUFLEDER (*Monatsh.*, 1901, 22, 700—706).—Red and yellow phosphorus may be either polymorphous or chemically different (isomeric or polymeric). If the two forms are polymorphous, the liquid forms must be identical, and molten yellow phosphorus or a concentrated solution should, on addition of red phosphorus (which is the stable form), change into the latter. Experiments show that such is not the case. A saturated solution of yellow phosphorus in carbon disulphide sown with red phosphorus shows no perceptible change, and, on lowering the temperature, yellow phosphorus separates. Similar molten yellow phosphorus at 200°, to which red phosphorus has been added, does not change. The two forms are not polymorphous, but chemically different.

K. J. P. O.

**Metaphosphates.** By ARTHUR WEISLER (*Zeit. anorg. Chem.*, 1901, 28, 177—209).—Sodium trimetaphosphate, when prepared according to Fleitmann's and Henneberg's methods, and when prepared from sodium hydrogen phosphate and ammonium nitrate according to Knorre's method (*Abstr.*, 1900, ii, 651), has an electrical conductivity which indicates that it is a salt of a tribasic acid. The trimetaphosphate, in aqueous solution (1/32*N*), is not altered by boiling; neither orthophosphate nor pyrophosphate is formed.

Barium, manganese, and silver trimetaphosphates are described; of these the manganese salt has an electrical conductivity corresponding with that required for a salt of a tribasic acid. The other two salts are too insoluble for the determination of their electrical conductivities.

Copper trimetaphosphate could not be obtained from sodium trimetaphosphate, the product being a pyrophosphate of the formula  $\text{Cu}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ . In the case of zinc, a sodium zinc pyrophosphate is produced. The sodium cadmium trimetaphosphate,  $\text{CdNa}_4(\text{PO}_3)_6 \cdot 4\text{H}_2\text{O}$ , is obtained by adding cadmium iodide to the sodium salt.

Sodium hexametaphosphate, prepared from sodium pyrophosphate according to Knorre's method (*Zeit. angew. Chem.*, 1892, 641), has an electric conductivity  $\lambda_{32} = 31.2$ , which is evidence that the salt has a more complicated composition than the trimetaphosphate ( $\lambda_{32} = 89.4$ ). The hexametaphosphate is easily decomposed in aqueous solution and when heated at 40° yields the pyrophosphate.

E. C. R.



**Chemical Reactions produced by Radium.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1901, 133, 659—664).—The radiations from radium decompose iodic acid, with liberation of iodine, and also decompose nitric acid, the changes in both cases being endothermic. They do not, however, promote the oxidation of oxalic acid, or the conversion of sulphur into the variety insoluble in carbon disulphide, nor do they, like the silent electric discharge, cause the polymerisation of acetylene. The author confirms the statement that the rays gradually turn glass black, a change which he attributes to the reduction of lead compounds to the metallic state, and has also observed the production of a violet colour similar to that produced by the action of light on certain glasses containing manganese. It would seem, therefore, that the radiations cause a reduction and an oxidation simultaneously, and possibly the one change is consequent on the other.

C. H. B.

**Action of Bromine on Metallic Silver in the Light and in Darkness.** By V. VON CORDIER (*Monatsh.*, 1901, 22, 707—716. Compare Abstr., 1900, ii, 343, 723).—By use of a specially constructed apparatus, the action of bromine on metallic silver illuminated by an arc lamp, an incandescent gas lamp, or diffused daylight, and in darkness was investigated. Whilst light assists the combination of silver and chlorine (*loc. cit.*), it hinders that of silver and bromine. Bromine is not given off in the light from silver bromide in the presence of carbon dioxide.

K. J. P. O.

**Action of Hydrogen Peroxide on Silver Oxide.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1901, 133, 555—569).—The author has investigated in the calorimeter the action of several acids on (1) silver oxide, and (2) silver oxide which had been treated with hydrogen peroxide. The development of heat differs considerably in the two cases, both in rate and amount, and the results, which are described in detail, confirm the author's previous conclusions as to the formation of a higher oxide of silver (Abstr., 1899, ii, 149).

C. H. B.

**Reduction of Copper by Solutions of Ferrous Salts.** By H. C. BIDDLE (*Amer. Chem. J.*, 1901, 26, 377—382).—The precipitation of copper by solutions of ferrous salts is a reversible action, the direction of which in any case is determined by the relative concentration of the ferrous, ferric, and copper (cuprous and cupric) ions. This statement is justified by the following experimental evidence. In a solution containing an appreciable quantity of ferric ions, or in which these would be formed in the course of the reaction, copper is not deposited; this is shown by the fact that ferrous chloride and sulphate are incapable of reducing the corresponding copper salts. In a solution containing a few ferric ions, and in which the reaction does not cause an appreciable increase of them, a sufficient concentration of ferrous and copper ions will produce the deposition of copper. The tendency of ferrous salts to reduce those of copper is shown by the precipitation of cuprous thiocyanate when ammonium thiocyanate is

added to a solution of ferrous and cupric chlorides. From a mixture of ferrous and cupric hydroxides, crystals of cuprous oxide slowly separate. When an excess of ammonium carbonate is added to a solution of ferrous and cupric chlorides, a yellow liquid is obtained which gradually deposits a mirror of metallic copper. If a solution of cupric and ferrous chlorides is treated with sodium carbonate in slight excess or with potassium hydrogen carbonate, reduction slowly takes place with loss of carbon dioxide and formation of basic ferric carbonate and copper.

E. G.

**Mixed Crystals of Copper Sulphate and Zinc Sulphate.** By H. W. FOOTE (*Amer. Chem. J.*, 1901, 26, 418—428).—It is well known that from solutions of copper sulphate containing zinc sulphate an isomorphous mixture of triclinic crystals separates consisting of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  together with a smaller quantity of  $\text{ZnSO}_4 \cdot 5\text{H}_2\text{O}$ . As the quantity of zinc sulphate is increased in the solution, an isomorphous mixture of monoclinic crystals is obtained containing  $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , and in presence of a still larger proportion of zinc sulphate, rhombic crystals of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  with a small amount of  $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$  are produced. It has been shown by van't Hoff, from theoretical considerations, that the composition of mixed crystals at their 'mixing limit' (which represents the composition of mixed crystals of one salt with a maximum of another) ought to be a function of the temperature; the same conclusion is arrived at by application of the phase rule.

The authors have carried out experiments on the 'mixing limit' of copper sulphate and zinc sulphate at 12°, 25°, 35°, 40°, and 45°, which confirm the accuracy of the above assumption, and also show that whilst the composition of mixed crystals varies with the temperature, the salts mentioned do not form completely isomorphous crystals between 12° and 56°. It is also found that in solutions yielding two forms of crystals, the amount of copper sulphate in solution remains nearly constant, whilst the quantity of zinc sulphate increases considerably with rising temperature.

E. G.

**Cuprous Chloride.** By MAX GRÖGER (*Zeit. anorg. Chem.*, 1901, 28, 154—161).—When cuprous chloride is treated with water in an atmosphere of hydrogen or carbon dioxide, the chlorine passes almost completely into solution and a dark red residue, consisting of cuprous oxide and copper, is left. The separation of the copper is due to the action of light, for when the extraction is carried out in the dark the residue is almost pure cuprous oxide. Water acting on cuprous chloride in presence of a little air gives an orange-red residue of cuprous oxide mixed with about 5 per cent. of basic cupric chloride. The amount of cupric compound left in the residue is always small, showing that most of the oxidation product of the cuprous chloride passes into solution. By the action of water and air sufficient for the complete oxidation, a residue was obtained which had the composition  $3\text{CuO} \cdot \text{CuCl}_2 \cdot 4\text{H}_2\text{O}$ . The primary action is the hydrolysis of the cuprous chloride, and the liberated hydrochloric acid, in presence of oxygen, acts upon more cuprous chloride forming the cupric com-

pound. Secondly, the cupric chloride reacts with the cuprous oxide (hydrolytic product) forming cuprous chloride again and basic cupric chloride.

Very dilute hydrochloric acid in an atmosphere of carbon dioxide changes the colour of cuprous chloride through green, almost black, to a dark copper brown. The residue in this case consists of metallic copper formed by the decomposition  $\text{Cu}_2\text{Cl}_2 = \text{Cu} + \text{CuCl}_2$ ; but as copper is deposited on the cuprous chloride it protects this from total decomposition. Cuprous chloride in a solution of cupric chloride, when protected from the action of the air, remains perfectly white even in sunlight, showing that cupric chloride prevents the direct decomposition of the cuprous compound.

Perfectly dry cuprous chloride remains unchanged in the air and light has no effect upon it.

The method recommended for the preparation of cuprous chloride is to dissolve 42 grams of cupric chloride in 200 c.c. of hydrochloric acid of sp. gr. 1.175 and 100 c.c. of water, and heat the solution with copper foil on the water-bath until it is decolorised. The solution is then poured into 2 litres of water, the precipitate filtered (in diffused light) and washed, first with dilute sulphuric acid (1 : 20), then with absolute alcohol, drained as dry as possible on the pump and dried quickly in the water-oven.

J. McC.

**Mercury Oxychlorides.** By N. TARUGI (*Gazzetta*, 1901, 31, ii, 313—320).—The author has examined the various oxychlorides of mercury described by different authors, and finds that, without exception, they consist of mixtures, in indefinite proportions, of mercuric oxide and chloride. The three compounds described below are therefore the first oxychlorides of mercury obtained.

The *oxychloride*,  $\text{HgCl}_2 \cdot 3\text{HgO}$ , is obtained by adding small cubes of perfectly white statuary marble of a sugar-like structure into saturated aqueous mercuric chloride at 15°. After remaining for 15—20 days in diffused light, the liquid deposits the oxychloride in small, yellow crystals which continue to increase in number and size, and are separated, washed with water, and dried in a vacuum. When heated or when boiled with water or alkali solution, the oxychloride decomposes into its constituents, whilst dilute nitric acid converts it into a white, amorphous powder.

If the saturated mercuric chloride solution is diluted with twice its volume of water and treated as before, an *oxychloride* of the formula  $\text{HgCl}_2 \cdot 2\text{HgO}$ , is obtained in very thin, black crystals; whilst if three volumes of water are added to the saturated mercuric chloride solution, a *compound* of the composition  $\text{HgCl}_2 \cdot \text{HgO}$ , is produced in very thin, red crystals. These two oxychlorides have the same chemical properties as the first described.

T. H. P.

**Alkali Double Nitrites of Mercury and Zinc.** By ARTHUR ROSENHEIM and KURT OPPENHEIM (*Zeit. anorg. Chem.*, 1901, 28, 171—174).—Mercuric nitrate, when treated with a concentrated solution of potassium nitrite, dissolves and the solution becomes warm. Mercuric oxide separates out and from the filtrate yellow crystals

of *potassium mercury nitrite* of the composition  $K_3Hg(NO_2)_5 \cdot H_2O$  are deposited. The salt crystallises in rhombic forms [ $a:b:c = 0.8594:1:0.7581$ ] and is soluble in cold water without decomposition.

If the solution of this salt contains a slight excess of potassium nitrite, ill-defined crystals of the compound  $KHg(NO_2)_3$  are formed.

*Sodium mercury nitrite*,  $Na_2Hg(NO_2)_4$ , has been prepared by recrystallising the product obtained by the action of a concentrated solution of sodium nitrite on mercuric nitrate.

*Potassium zinc nitrite*,  $K_3Zn(NO_2)_5 \cdot 3H_2O$  is produced when nitrous acid is passed into a solution of potassium nitrite containing zinc hydroxide in suspension. It forms very hygroscopic, yellow crystals.

J. McC.

**Copper-Aluminium Alloys.** By LÉON GUILLET (*Compt. rend.*, 1901, 133, 684—686).—The author has prepared various copper aluminium alloys by heating pure cupric oxide with granular aluminium in proportions varying from those which should yield pure copper to those which should yield the alloy  $CuAl_4$ . By treating the products with acids, he has isolated three distinctly crystalline, definite alloys,  $Cu_3Al$ ,  $CuAl_2$ , and  $CuAl$ , the last being mixed with a small quantity of copper aluminium silicide.

C. H. B.

**Compounds of Aluminium Bromide with Bromine and Carbon Disulphide.** II. By WLADIMIR A. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 429—432. Compare Abstr., 1901, ii, 316).—The compound of the composition  $AlBr_3 \cdot Br_4 \cdot CS_2$ , previously described (*loc. cit.*) by the author as obtained by the action of bromine on a carbon disulphide solution of aluminium bromide, is only formed when the bromine is employed in excess. If, however, to a well-cooled solution of aluminium bromide (1 mol.) in carbon disulphide a quantity of bromine not greater than 1 atomic proportion is added slowly in drops, an almost theoretical yield of an oily compound is obtained, having the composition  $2AlBr_3 \cdot Br_4 \cdot CS_2$ . When left in a warm place or when shaken repeatedly with carbon disulphide, the oil deposits a brownish, crystalline mass, which, when dry, melts at about  $80^\circ$  and begins to dissociate into aluminium bromide and  $CS_2 \cdot Br_4$  at about  $100^\circ$ ; dissociation also occurs under the influence of even traces of moisture. The compound is soluble in ether or benzene.

T. H. P.

**The Reduction of Alumina by Calcium Carbide.** By SAMUEL A. TUCKER and HERBERT R. MOODY (*J. Soc. Chem. Ind.*, 1901, 20, 970—971).—In the electric furnace, aluminium oxide is not reduced by carbon, but if lime is added calcium carbide is formed and this reduces the alumina. Calcium carbide reduces alumina and the yield of aluminium is increased by the presence of free carbon. The heat should not be applied longer than 15 minutes, for after that time aluminium carbide is formed.

J. McC.

**Periodic System and the Properties of Inorganic Compounds.** III. **The Solubility of Alums as a Function of Two Variables.** By JAMES LOCKE (*Amer. Chem. J.*, 1901, 26, 332—345).—The author

has previously determined the solubility at  $25^{\circ}$  of the alums of aluminium, vanadium, chromium and iron severally with ammonium, thallium, rubidium and caesium (Abstr., 1901, ii, 656). When the solubilities of these 16 compounds expressed in gram-mols. per litre of water are plotted as a function of the atomic weights of the trivalent metals, a figure of remarkable regularity is obtained, from a consideration of which it is evident that the lines joining the solubility points of the successive univalent metals with two given trivalent metals have approximately a common point of intersection. It must be assumed, therefore, that the points representing the solubilities stand in fixed mathematical relation to one another. Hence it is shown that if the difference in the solubility of the alums of a given trivalent metal with two alkali metals is termed "the increment of solubility for the latter," the general law is obtained that "the ratio between the increments of solubility of the corresponding alums of two trivalent metals for any two alkali metals is constant." The accuracy of this law is fully confirmed by observation. A general equation for the solubility of any of the sixteen alums is deduced from this law, all the terms of which can be referred to two variables, one applying to the trivalent element in the compound and the other to the univalent metal. Determinations made at other temperatures than  $25^{\circ}$  indicate that it will be possible to derive a general solubility formula for all temperatures.

E. G.

**The Reaction of Sodium Thiosulphate with Potassium Permanganate.** By A. ÅLANDER (*Zeit. anal. Chem.*, 1901, 40, 574—577).—Both qualitative and quantitative proofs are given that in alkaline solutions the reaction  $8\text{KMnO}_4 + 3\text{Na}_2\text{S}_2\text{O}_3 = 3\text{Na}_2\text{SO}_4 + 3\text{K}_2\text{SO}_4 + 8\text{MnO}_2 + \text{K}_2\text{O}$  is the principal one, but that a small quantity of the thiosulphate (about 1.3 per cent.) is oxidised only to tetrathionate.

M. J. S.

**Separation of Iron.** By PAUL NICOLARDOT (*Compt. rend.*, 1901, 133, 686—688).—When ferric chloride is heated at  $125^{\circ}$  it is converted into a complex compound in which the ratio of iron to chlorine is 1:1, whilst the corresponding sulphate is insoluble. The iron alloy (1 gram) or compound is dissolved in aqua regia, the nitric acid expelled, and the liquid evaporated to dryness and heated at  $125^{\circ}$  for 4 hours. It is then diluted with water to 500 c.c., heated to boiling, and about 1 gram. of ammonium sulphate added. After boiling for about 15 minutes, the very finely divided precipitate is filtered off. If mercury or cadmium is present, the substance cannot be heated at  $125^{\circ}$  without loss, and therefore the liquid is exactly neutralised with ammonia, mixed with ammonium sulphate, boiled, and filtered. It is again mixed with ammonia until a slight precipitate is formed and again boiled, when the whole of the iron is precipitated. Selenates, phosphates, arsenates, vanadates, and molybdates precipitate iron in a similar manner, and the iron is readily separated from the precipitate by fusion with an oxidising mixture or an alkali.

C. H. B.

**Ferric Oxide and Hydroxides.** By OTTO RUFF (*Ber.*, 1901, 34, 3417—3430. Compare Tommasi, *Ber.*, 1879, 12, 1929, 2334).—The red, colloidal ferric hydroxide may be converted into true hydrates

by the aid of considerable pressure under water. At a temperature of  $42.5^\circ$ , it yields brown ironstone, at  $42.5$ — $62.5^\circ$ , g $\ddot{o}$ thite, and at higher temperatures, hydroh $\ddot{a}$ ematite. Yellow ferric hydroxide is not a true colloid, as its percentage of water under high pressure does not vary between temperatures of  $40^\circ$  and  $70^\circ$ .

The red hydroxide appears to lose water at the ordinary atmospheric temperature and pressure and, at the same time, but somewhat more slowly, takes up water and becomes converted into brown ironstone, the only stable hydrate under ordinary conditions. J. J. S.

**Influence of the Separation of Sulphur on the Precipitation of Iron Salts.** By A. COPPADORO (*Gazzetta*, 1901, 31, ii, 217—221).—When hydrogen sulphide is passed through an acidified solution of a ferric salt, a precipitate of sulphur is formed containing small quantities of iron compounds, which the most exhaustive washing is incapable of removing. By dissolving the sulphur from the dried precipitate by means of carbon disulphide, however, the author has succeeded in determining the amount of iron enclosed in the precipitate. He finds that the quantity of iron is proportional to that of the ferric salt taken and to that of the precipitated sulphur, but is independent of the amount of acid added to the solution and of the time during which the hydrogen sulphide is kept passing through the liquid. If a precipitate of sulphur is produced in a solution of a ferrous salt, for example, by the addition of thiosulphate and acid, the precipitate is found to contain iron. The author suggests that possibly the presence of iron in these precipitates is connected with Graham's observation that when solutions of two colloids are mixed they are precipitated together. T. H. P.

**Crystallographic Examination of some Luteocobaltic Salts.** By TIMOTHÉE KLOBB (*Chem. Centr.*, 1901, ii, 970; from *Bull. Soc. franç. Min.*, 24, 307—322. Compare Abstr., 1901, ii, 103).—Luteocobaltic selenate,  $\text{Co}(\text{NH}_3)_6(\text{SeO}_4)_3 \cdot 5\text{H}_2\text{O}$ , prepared by neutralising luteocobaltic hydroxide with selenic acid and slowly evaporating the solution, separates in thick, brownish-yellow, monoclinic crystals [ $a : b : c = 1.1350 : 1 : 1.4023$ ,  $ac = 90^\circ 35'$ ]. Luteocobaltic sulphate,  $\text{Co}(\text{NH}_3)_6(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ , forms lustrous, monoclinic crystals [ $a : b : c = 1.1230 : 1 : 1.4143$ ,  $ac = 90^\circ 18'$ ]. Luteocobaltic hydrogen sulphate,  $2\text{Co}(\text{NH}_3)_6(\text{SO}_4)_3 \cdot 5\text{H}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , obtained by adding sulphuric acid to an aqueous solution of the normal salt, crystallises in small, rhombic octahedra [ $a : b : c = 0.99913 : 1 : 1.0006$ ] and is decomposed by water. Luteocobaltic hydrogen selenate,  $\text{Co}(\text{NH}_3)_6(\text{SeO}_4)_3 \cdot \text{H}_2\text{SeO}_4 \cdot 5\text{H}_2\text{O}$ , prepared by adding excess of selenic acid to luteocobaltic hydroxide or to the normal selenate, crystallises in triclinic crystals, often twinned [ $a : b : c = 0.84550 : 1 : 0.47285$ ,  $bc = 88^\circ 50'$ ,  $ac = 80^\circ 50'$ ,  $ab = 86^\circ 47'$ ], and is not decomposed by water. Luteocobaltic chlorosulphate, obtained from cobalt chloride or sulphate or by treating luteocobaltic chloride with sulphuric acid or a sulphate, is rhombic [ $a : b : c = 0.99855 : 1 : 1.0538$ ]. Luteocobaltic chloroselenate is rhombic [ $a : b : c = 0.99869 : 1 : 1.0563$ ]. Luteocobaltic ammonium sulphate,  $[\text{Co}(\text{NH}_3)_6]_{12}(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$ , prepared by crystallising luteocobaltic sulphate in presence of ammonia,

separates in rhombic octahedra or thick plates. When moistened with water, the crystals become opaque, but in concentrated ammonium sulphate solution they remain transparent and ultimately dissolve. Luteocobaltic ammonium selenate,  $[\text{Co}(\text{NH}_3)_6]_2(\text{SeO}_4)_3 \cdot (\text{NH}_4)_2\text{SeO}_4 \cdot 8\text{H}_2\text{O}$ , obtained by neutralising a solution of luteocobaltic hydrogen selenate with ammonia, is isomorphous with the preceding salt [ $a:b:c = 0.95953:1:1.2024$ ]. After the separation of this hydrate, a hydrate crystallising with  $4\text{H}_2\text{O}$  crystallises out in large, monoclinic prisms [ $a:b:c = 1.4285:1:0.64688$ ,  $ac = 94^\circ 42'$ ]. Luteocobaltic chloroammonium sulphate,  $[\text{Co}(\text{NH}_3)_6]_4(\text{SO}_4)_3\text{Cl}_2 \cdot 3(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , prepared by evaporating a solution of luteocobaltic chlorosulphate with an excess of ammonium sulphate, crystallises in octahedra and is decomposed by water. E. W. W.

**Crystallographic Study of Alvisi's Luteocobaltiammine Perchlorates.** By FEDERICO MILLOSEVICH (*Gazzetta*, 1901, 31, ii, 285).—Luteocobaltiammonium diperchlorate chloride,  $\text{Co}(\text{NH}_3)_6\text{Cl}(\text{ClO}_4)_2$ , forms rhombohedral, orange-yellow crystals,  $\alpha = 70^\circ 41'$ .

Luteocobaltiammonium perchlorate,  $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$ , gives orange-yellow crystals of the cubic system. T. H. P.

**Researches on Perchlorates. Luteocobaltiammine Perchlorates and Observations on Metallo-Ammoniums. I.** By UGO ALVISI (*Gazzetta*, 1901, 31, ii, 289—301).—The author has prepared various luteocobaltiammine perchlorates and gives the methods used by him for their analysis.

*Luteocobaltiammonium diperchlorate chloride*,  $\text{Co}(\text{NH}_3)_6\text{Cl}(\text{ClO}_4)_2$ , prepared by the interaction of cold saturated solutions of ammonium perchlorate (3 mols.) and luteocobaltiammine chloride (1 mol.), crystallises from water in hexagonal, yellow plates having a pearly lustre; when rapidly heated, it gradually loses ammonia, and at about  $188^\circ$  explodes, water vapour, chlorine, and nitrogen being evolved and cobalt oxide and chlorides left.

*Luteocobaltiammonium perchlorate*,  $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$  is prepared (1) by heating aqueous cobalt perchlorate with excess of ammonium perchlorate and ammonia and adding potassium (or better sodium) permanganate until the liquid assumes an intense, golden-yellow coloration; or (2) by heating a solution of cobalt perchlorate with lead dioxide, ammonia, and excess of ammonium perchlorate until the filtered liquid becomes intensely orange-yellow in colour. It crystallises from water in orange-yellow octahedra belonging to the cubic system and with hydrochloric acid yields the diperchlorate chloride just described.

Theoretical considerations are put forward by the author as to the mode of combination of nitrogen in the cobaltiammonium compounds with the other elements present. T. H. P.

**Cause of the Brown Coloration of Ammonium Sulphide in Presence of a Nickel Salt.** By UBALDO ANTONY and G. MAGRI (*Gazzetta*, 1901, 31, ii, 265—274).—When hydrogen sulphide or ammonium polysulphide solution is added to an ammoniacal solution

of nickel acetate in quantity insufficient to precipitate all the nickel as sulphide, the precipitate obtained has the composition  $\text{NiS}$ , and in the latter case is mixed with sulphur. When, however, an excess of ammonium polysulphide is added to an ammoniacal nickel solution, the precipitate formed is of very variable composition but the dark liquid always contains a sulphide of the composition  $\text{NiS}_4$ . This sulphide, which is obtained as a black powder, is only slightly attacked by hydrochloric acid but reacts vigorously with nitric acid, sulphur being liberated. In an atmosphere of carbon dioxide, it loses sulphur at  $300^\circ$ , being converted into nickel sulphide, whilst when heated in water in presence of air it slowly oxidises, giving nickel sulphate and sulphuric acid. Hydrogen sulphide solution has no action on it, but it is dissolved by a solution of sulphur or ammonium polysulphides giving a brown liquid. With ammonia solution, it yields an azure-blue liquid containing nickel, but all the sulphur is deposited in a very fine state of division. Measurements of the electrical conductivity of solutions of nickel tetrasulphide in ammonium sulphide show that the nickel salt is not present in a state of true solution or in a really colloidal condition, the author regarding it as existing in an intermediate state.

T. H. P.

#### Action of Sodium Thiosulphate on certain Metallic Salts.

By FRANZ FAKTOR (*Chem. Centr.*, 1901, ii, 878; from *Pharm. Post*, 34, 485—487. Compare Abstr., 1900, ii, 598, 627, 688, 691, and 692).—Ammonium molybdate is reduced by a solution of sodium thiosulphate, forming molybdenum trioxide and the hydrate of the dioxide,  $\text{MoO}_3 \cdot 3\text{H}_2\text{O}$ , whilst sodium tungstate, when warmed with sodium thiosulphate and a small quantity of nitric acid, yields tungsten dioxide, trioxide, and heptoxide. By the action of sodium thiosulphate on uranyl nitrate, a yellow precipitate of *uranyl thiosulphate*,  $\text{UO}_2\text{S}_2\text{O}_3$ , is formed; the thiosulphate, on ignition, yields the green oxide,  $\text{U}_3\text{O}_8$ . *Beryllium thiosulphate*,  $\text{BeS}_2\text{O}_3 \cdot 11\text{H}_2\text{O}$ , is prepared from sodium thiosulphate and beryllium sulphate. Quinone is reduced by sodium thiosulphate, forming first quinhydrone and then quinol. By the action of sodium thiosulphate and hydrogen dioxide on manganese salts, a brown precipitate of manganese hydroxide is obtained; when treated in the same way, chromates are reduced to chromic hydroxide, cobalt salts give a black and nickel salts a pale green precipitate.

E. W. W.

**Two Phosphorus-Molybdenum Compounds.** By F. MAWROW (*Zeit. anorg. Chem.*, 1901, 28, 162—166).—On addition of hypophosphorous acid to a solution of ammonium molybdate in concentrated hydrochloric acid, a bluish-green solution is produced and a violet deposit with a coppery lustre obtained. This deposit is soluble in cold water, giving a green solution, which, on exposure to air, becomes blue. It is decomposed by alkali, forming a green precipitate. It is soluble in concentrated sulphuric acid with a blue colour, and on dilution a yellowish brown precipitate is formed. Heated on platinum foil, it explodes and leaves a grey residue. Its composition can be represented by  $\text{Mo}_5\text{O}_8(\text{H}_3\text{PO}_2)_7 \cdot 3\text{H}_2\text{O}$ .

On heating an aqueous solution of this, it becomes blue and on evaporating at  $90$ — $95^\circ$  a blue residue is obtained which is soluble in



water or alcohol with a blue colour and explodes when heated. Its composition is represented by  $\text{Mo}_5\text{O}_{13}(\text{H}_3\text{PO}_2)_8 \cdot \text{H}_2\text{O}$ . Both these compounds are strong reducing agents, indicating that the phosphorus is present in the condition of hypophosphorous acid. It is doubtful if the formulæ given are correct, but it is certain that the substances are not compounds of molybdic acid, but of a lower oxide of molybdenum.

The blue solution gives characteristic precipitates with salts of ammonium, barium, lead, and bismuth. J. McC.

**Behaviour of Hydrochloric Acid Solutions of Metastannic Acid towards Hydrogen Sulphide.** By GUNNER JÖRGENSEN (*Zeit. anorg. Chem.*, 1901, 28, 140—153).—Hydrogen sulphide gives with hydrochloric acid solutions of metastannic acid, precipitates which vary in composition according to the concentration of the hydrogen sulphide, the concentration of the hydrochloric acid, the temperature, and the time. At first, the precipitate consists for the greater part of metastannic acid mixed with a small quantity of stannic sulphide. When kept, the precipitate absorbs hydrogen sulphide slowly and only after a very long time (two months) does the composition correspond with that of stannic sulphide. Increase of the concentration of metastannic acid, or of hydrogen sulphide, or rise of temperature lead to an increase in the proportion of stannic sulphide formed. Increase of the concentration of hydrochloric acid diminishes the absorption of hydrogen sulphide. The rate of formation of the stannic sulphide is extremely slow and it decreases to a far greater extent than the law of mass action would indicate; this is possibly due to the formation of soluble thiostannate ions. J. McC.

**Thiocyanates of Quadrivalent Titanium.** By ARTHUR ROSENHEIM and ROBERT COHN (*Zeit. anorg. Chem.*, 1901, 28, 167—170). Compare this vol., ii, 244).—Thiocyanic acid solution dissolves large quantities of titanous acid, and on evaporation of the saturated solution in a vacuum over sulphuric acid a brownish-red, crystalline powder is obtained which is soluble in cold water, exhibits the reactions of thiocyanates, and possesses all the properties of a titanium salt. It has the composition  $\text{TiO}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$ .

A solution of titanous acid in thiocyanic acid, when mixed with potassium thiocyanate and evaporated over sulphuric acid, gives hygroscopic, deep red, rhombic crystals of  $\text{K}_3\text{TiO}(\text{SCN})_4 \cdot \text{H}_2\text{O}$ . This is soluble in cold water, but on standing it is decomposed with decolorisation. The corresponding ammonium, sodium, and barium salts have been obtained, but not quite pure.

The pyridine compound,  $(\text{C}_5\text{NH}_5)_2\text{H}_2\text{TiO}(\text{SCN})_4$ , as a purple precipitate, is obtained when a concentrated hydrochloric acid solution of pyridine in alcohol is added to a solution of thiocyanic and titanous acids. The precipitate can be recrystallised from the mother liquor and is then obtained in well-defined, bluish-black crystals.

The quinoline salt,  $(\text{C}_9\text{NH}_7)_2\text{H}_2\text{TiO}(\text{SCN})_4 \cdot 4\text{H}_2\text{O}$ , can be prepared in the same way. By recrystallisation from the mother liquor, it separates in deep red crystals, which could not be obtained pure but are probably anhydrous. J. McC.

**Fluorovanadium Compounds.** By PETR G. MELIKOFF and P. KASANEZKY (*Zeit. anorg. Chem.*, 1901, **28**, 242—254).—Potassium vanadium dioxyfluoride,  $\text{VO}_2\text{F}_2\cdot 2\text{KF}$ , when treated with successive portions of hydrogen peroxide, behaves like a compound of the constitution  $\text{VF}_3(\text{KO})_2$ . The fluorine is gradually replaced by oxygen, and orange to red crystalline compounds are obtained containing successively less fluorine, the final product of the reaction being pervanadate. The corresponding ammonium salt reacts in a similar manner.  
E. C. R.

**Preparation of Pure Stibine.** By KARL OLSZEWSKI (*Ber.*, 1901, **34**, 3592—3593).—With reference to the statements of Stock and Doht (*Abstr.*, 1901, ii, 556), the author points out that the phenomenon previously observed by him (*Abstr.*, 1886, 977) was a decomposition, not a dissociation, of liquid stibine, and that in his experiments air had access to the liquid. Stibine boils at about  $-18^\circ$ , probably somewhat lower than this.  
A. H.

**Gold Haloids.** By FELIX LENGFELD (*Amer. Chem. J.*, 1901, **26**, 324—332).—Aurous chloride is insoluble in water and dilute nitric acid, and is decomposed by strong nitric acid with production of auric chloride and gold. When nitric acid is added to an ammoniacal solution of the salt, a white, curdy, unstable precipitate is formed. If aurous chloride is added to solution of potassium bromide, gold separates, and a brownish-red liquid is obtained, containing potassium aurichloride and auribromide. It dissolves in a solution of sodium chloride with formation of an unstable double salt, probably  $\text{NaAuCl}_2$ .

Aurous bromide is insoluble in water and nitric or sulphuric acid, but dissolves in ammonia with partial decomposition; on addition of nitric acid to the ammoniacal solution, an unstable precipitate is produced. Potassium cyanide dissolves the salt without decomposition. Potassium bromide yields potassium auribromide and gold. With hydrobromic or hydrochloric acid, it is converted into bromoauric or chloroauric acid and gold. Both aurous chloride and bromide are slowly decomposed by ether, alcohol, or acetone.

Auroso-auric bromide (aurous auribromide), obtained by the action of bromine on gold, is a steel-blue substance, stable in the absence of water, but easily decomposed by water and many organic solvents.

Chloroauric and bromoauric acids form the compounds  $\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$ ,  $\text{HAuBr}_4\cdot 3\text{H}_2\text{O}$ , and  $\text{HAuBr}_4\cdot 6\text{H}_2\text{O}$ , but the compounds  $\text{HAuCl}_4\cdot 4\text{H}_2\text{O}$  and  $\text{HAuBr}_4\cdot 5\text{H}_2\text{O}$  probably do not exist.

When solutions of chloroauric acid and silver nitrate are mixed at  $0^\circ$ , a yellow precipitate is formed which rapidly darkens and decomposes. If an alcoholic solution of potassium aurichloride is shaken with silver carbonate, silver chloride and auric chloride are produced.

E. G.

## Mineralogical Chemistry.

**Fusibility of Minerals and their Solubility in Magmas.** By CORNELIUS DOELTER (*Chem. Centr.*, 1901, ii, 826—827; from *Tsch. Min. Mitth.*, 1901, 20, 307—330).—The results are given of detailed observations of the manner in which various minerals are attacked by molten magmas. As a rule, minerals with a very high melting point (quartz, corundum, olivine, leucite) are more sparingly soluble than those with a lower melting point (felspar, augite, mica). In general, however, the solubility of a mineral in a magma depends on the pressure, the temperature, and the chemical composition of the magma, as well as on the fusibility of the particular mineral. L. J. S.

**Retinite from Thessaly.** By CONSTANTIN ZENGELIS (*Chem. Centr.*, 1901, ii, 833; from *Tsch. Min. Mitth.*, 1901, 20, 356).—This retinite is yellowish-red, almost opaque, hard and readily combustible, sp. gr. 1.0023. At 290°, it softens and fuses with decomposition. Benzene dissolves 17.4 per cent. The following analysis corresponds with that required for the formula  $C_{10}H_{14}O$ :

C.	H.	S.	O.	Ash.	Moisture.
78.47	9.23	0.39	10.616	1.47	0.214

L. J. S.

**Calaverite.** By SAMUEL L. PENFIELD and W. E. FORD (*Amer. J. Sci.*, 1901, [iv], 12, 225—246. Compare Abstr., 1896, ii, 31).—A detailed crystallographic account is given of crystals of calaverite from Cripple Creek, Colorado. They are interpreted as being monoclinic and elongated in the direction of the axis of symmetry, but the faces have very high indices and do not fall into zones. The axial ratios,  $a:b:c = 1.6313:1:1.1449$ , axial angle,  $\beta = 89^\circ 47' \frac{1}{3}$ , and, twinning, resemble those of sylvanite, but calaverite differs from this mineral in having no distinct cleavage. The general formula  $(Au, Ag)Te_2$  expresses the chemical composition of both calaverite and sylvanite, but the latter contains more silver, and its formula approximates to  $AuAgTe_4$ . The following analyses are given of the material now described:

Au.	Ag.	Te.	Gangue.	Total.	Sp. gr.
40.99	1.74	[57.25]	0.02	100.00	9.328
42.77	0.40	[56.75]	0.08	100.00	9.388

The colour of the brightest calaverite crystals is silver-white, sometimes with a yellowish cast; it is not bronze-yellow as often described.

L. J. S.

**Monazite from New Granada.** By NICHOLAS J. BLUMAN (*Chem. News*, 1901, 84, 175).—A sample of reddish-brown colour, sp. gr. 6.001 and hardness 5, gave the following numbers on analysis:

$Co_2O_3$ .	$La_2O_3$ .	$ThO_2$ .	MnO.	CaO.	$SnO_2$ .	$P_2O_5$ .	Fe, Zn, S.	Total.
25.02	22.41	18.00	1.21	2.13	3.00	28.23	traces	100.00

D. A. L.

**Triplite from Moravia and its Decomposition Products.** By FRANTIŠEK KOVÁŘ and FR. SLAVIK (*Jahrb. Min.*, 1901, i, Ref., 354—356; from *Verh. geol. Reichsanst.*, 1900, 397—404. Compare Abstr., 1901, ii, 248).—Cleavage masses of triplite, more or less altered, occur in large nests in pegmatite at Wien and Cyrillhof in Moravia. The optical characters and the following analyses are given: I and II are of weathered material from Wien, sp. gr. 3·901; calculating the iron as ferrous, these agree with the usual formula,  $(\text{Mn, Fe, Mg})_2\text{PO}_4(\text{F, OH})$ . III is of fairly fresh material and IV of much weathered material from Cyrillhof; the latter decomposes hydrochloric acid with the liberation of much chlorine.

Further alteration of the material results in the formation of a cellular mass of dufrenite and hydroxides of iron and manganese with a colourless hydrated phosphate of iron and manganese: analysis of this mixture gave VI. The dufrenite, separated as far as possible from the other substances, gave V, agreeing with the usual formula  $\text{Fe}_2(\text{OH})_3\text{PO}_4$ . The insoluble residue is shown by analysis and microscopical examination to consist of quartz, feldspar and muscovite.

	I.	II.	III.	IV.	V.	VI.
$\text{Fe}_2\text{O}_3$ .....	2·80	4·26	7·78	37·08	56·69	5·56
$\text{FeO}$ .....	26·10	24·31	33·37	—	—	41·80
$\text{Mn}_2\text{O}_3$ .....	—	—	—	16·24	1·48	—
$\text{MnO}$ .....	29·17	29·85	17·92	—	—	2·87
$\text{Al}_2\text{O}_3$ .....	—	—	—	0·35	0·36	0·13
$\text{CaO}$ .....	0·49	0·56	1·27	1·68	0·60	0·47
$\text{MgO}$ .....	4·58	4·74	0·40	0·56	0·23	0·12
Alkalis .....	—	—	0·19	0·63	—	—
$\text{P}_2\text{O}_5$ .....	31·67	30·89	32·44	17·56	29·02	31·31
$\text{CO}_2$ .....	trace	0·59	—	—	—	—
$\text{H}_2\text{O}$ .....	4·16	4·20	4·48	13·68	9·85	11·36
F .....	1·11	trace	0·88	—	—	—
Insol. ....	0·84	0·35	2·37	13·35	2·19	7·26
Total (less O for F).	100·45	99·75	100·73	101·13	100·42	100·88

The first stage in the alteration of the triplite is the replacement of fluorine by hydroxyl with the formation of triploidite. This is then oxidised and decomposed with the separation of hydroxides of iron and manganese along cracks, and finally yields the mixture of dufrenite, &c. Near the nests of triplite, the quartz of the pegmatite is represented only by empty cavities, and it is suggested that this mineral has been removed by the fluorine set free on the alteration of the triplite.

L. J. S.

**Emerald and Beryl from the Uralian Emerald Mines.** By PETR A. ZEMJATSCHENSKY (*Jahrb. Min.*, 1901, ii, Ref., 190—191; from *Trav. Soc. Nat. St. Petersburg*, 1900, 29, 1—19).—The emerald mines on the Takowaja river, 85 versts north-east of Ekaterinburg, have, since 1832, yielded fair amounts of emerald, beryl, phenakite and alexandrite. The emeralds are embedded in a dark mica-schist, or

occur, intergrown with tourmaline and felspar, in masses of quartz and felspar in the mica-schist; they are usually cloudy and enclose scales of mica, whilst along the frequent fractures felspar is deposited. The crystals have a zonal structure and are optically anomalous. Analyses I—III are of pale colour emerald, and IV—V of the dark brown mica in which they are embedded.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	BeO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	Mn <sub>2</sub> O <sub>4</sub>	Loss on ignition.	Total.
I.	66·65	18·43	trace	12·9	—	—	—	—	2·19	100·17
II.	66·96	18·58	—	13·1	—	—	—	—	2·1	100·74
III.	65·95	18·95	trace	12·89	—	—	—	—	2·20	99·99
IV.	40·20	26·22	13·31	—	6·69	10·44	0·87	trace	1·81	99·55
V.	40·12	26·19	13·50	—	6·10	10·23	0·80	—	1·87	98·81

L. J. S.

**Minerals from the Ilmen Mountains.** By P. SUSCHTSCHINSKY (*Jahrb. Min.*, 1901, i, Ref., 361—363; ii, Ref., 205—206; from *Trav. Soc. Nat. St. Petersburg*, 1900, 29, 21—46).—Minerals from the æschynite, aquamarine and zircon mines, near Miask, are described. Aquamarine gave, on analysis, the results under I. Black, rhombic dodecahedra of garnet in mica-slate gave II. Dark green crystals of ægirine-augite from druses in gneiss gave III (anal. by Antipoff).

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	BeO	CaO	MgO	Na <sub>2</sub> O	H <sub>2</sub> O	Total.
I.	66·02	18·81	—	—	13·27	—	—	—	1·45	99·55
II.	35·34	19·51	—	40·20	—	4·91	—	—	—	99·96
III.	50·58	5·47	3·92	23·18	—	3·85	2·19	8·17	—	97·36

L. J. S.

**Composition of Plagioclase.** By W. TARASSENKO (*Jahrb. Min.*, 1901, ii, Ref., 180—189; from *Mem. Nat. Soc. Kieff [Russ.]*, 1900, 16, 365—496. Compare Abstr., 1900, ii, 354).—The plagioclase of labradorite-rocks from (I) Selistsche (Gov. Volhynia) and (II) Gorodistsche (Gov. Kieff) was separated into several portions according to sp. gr. and each portion examined in detail. The eleven analyses, of which the means are given below, differ among themselves for each felspar only within the limits of errors of observation. The variation in the sp. gr. is attributed to the porosity of the material, due to the presence of fluid enclosures, cleavage cracks, &c.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Sp. gr.	Formula.
I.	55·28	28·27	10·18	5·17	1·10	2·647—2·710	Ab <sub>1</sub> An <sub>1</sub>
II.	53·05	29·77	12·08	4·30	0·80	2·697—2·756	Ab <sub>2</sub> An <sub>3</sub>

It is concluded that the plagioclases are not isomorphous mixtures, but compounds of the albite and anorthite molecules in definite proportions.

L. J. S.

**Sodalite from Viterbo.** By FERRUCCIO ZAMBONINI (*Jahrb. Min.*, 1901, ii, Ref., 19; from *Riv. Min. Crist. Ital.*, 1900, 24, 13).—Small crystals of sodalite from an "erratic block" at S. Sisto, near Viterbo, gave, on analysis:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	CaO	Cl	H <sub>2</sub> O	Total (less O for Cl).
36·60	34·26	1·85	17·75	0·90	4·31	5·14	99·84

L. J. S.

[Amphibole in] Soda-syenite from Miask. By ARRIEN JOHNSEN (*Jahrb. Min.*, 1901, ii, 117—127).—Descriptions are given of five rocks of the soda-syenite group from Miask in the Urals. One of these, called an ægirine-augite-soda-syenite, consists of albite, a little microcline, ægirine-augite, and a peculiar amphibole. This amphibole is pleochroic and has a wide angle of optical extinction ( $\epsilon : c = 36^\circ$ ); sp. gr. 3·15; an approximate analysis gave the following results:

SiO <sub>2</sub> (+TiO <sub>2</sub> ?).	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	MgO.	CaO.
58·50	12·38	14·32	4·79	3·16	4·30	0·92
		Na <sub>2</sub> O.	K <sub>2</sub> O.	Total.		
		4·09	0·48	102·94		

It appears to be intermediate between riebeckite and glaucophane.  
L. J. S.

Andalusite from the Rhætian Alps. By AUGUST GRAMANN (*Jahrb. Min.*, 1901, ii, Ref., 193—197; from separate publ. Zürich, 1899, 57 pp.).—At several localities in the Flüela and Scaletta districts in Switzerland, crystals of andalusite occur with cordierite, kyanite, sillimanite, muscovite, biotite, orthoclase, pericline, &c., in quartz lenticles in biotite-gneiss, but not in the gneiss itself. The sp. gr. of the andalusite is lower than usual, being 3·0532—3·0829. The colour is peach-blossom-red or violet, and the crystals have sometimes a darker coloured kernel. The colouring matter appears to be TiO<sub>2</sub> (rutile) rather than Ti<sub>2</sub>O<sub>3</sub>. The extremes of five analyses are:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> (+FeO).	Fe <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O.
33·76—34·71	63·93—64·69	Nil—0·44	0·49—1·78

The alteration product of the andalusite is a white, scaly, sericitic material containing much quartz and carbonates. By the aggregation of numerous scales of this secondary sericite, large plates of muscovite are formed, analysis of which gave the following results, agreeing with those required for the formula 4H<sub>2</sub>O, K<sub>2</sub>O, (Ca, Mg)O, 6Al<sub>2</sub>O<sub>3</sub>, 10SiO<sub>2</sub>:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	MgO.	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
43·09	42·16	0·29	2·54	6·79	trace.	5·11	99·98

L. J. S.

Fire-clay from Moravia. By FRANTIŠEK KOVÁŘ and ANT. HAŠKOVEC (*Jahrb. Min.*, 1901, ii, Ref., 226; from *Zeit. chem. Ind. Prag.*, 1899, 3 pp.).—Beds of fire-clay occur in the Quader sandstone at Vranová near Kunststadt. Analysis I is of whitish, and II, of dark greyish, more sandy, material.

SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Alkalis.	SO <sub>3</sub> .	Loss on ignition.	Total.
I. 52·42	trace	33·56	1·17	0·77	0·38	1·28	—	10·84	100·42
II. 52·11	0·17	27·73	5·92	0·91	0·57	1·07	0·21	12·78	100·47

L. J. S.

**Separation of Titaniferous Iron Ores in Basic Igneous Rocks** By JOHAN H. L. VOGT (*Chem. Centr.*, 1901, ii, 829; from *Zeit. prakt. Geol.*, 1901, 289—296. Compare Abstr., 1900, ii, 63; 1901, ii, 319).—A graphic representation of analyses shows that as concentration takes place, a decrease in silica is accompanied by a decrease in alumina and alkalis and an increase in titanium and iron oxides, while the variations in the lime show no regularity. Very advanced stages in the differentiation cannot be explained by a simple addition or subtraction of material, since, with varying conditions, the processes of differentiation are more or less changed as they proceed. In all probability, the differentiation is effected by the transference of a dissolved constituent in a solvent; the former being the bulk of the titanium and iron oxides and magnesia, and the latter a part of the silica with alumina, lime, and alkalis. The materials are concentrated in the same order in which they crystallise out from the magma, namely: (1) apatite; (2) sulphides; (3) titanium and iron oxides with spinel; (4) ferromagnesian silicates. Cases are, however, known in which all of these may be concentrated together. L. J. S.

**A South Australian Meteorite.** By GEORGE A. GOYDER (*Trans. Roy. Soc. South Australia*, 1901, 25, 14).—This iron, of which the weight is  $7\frac{1}{2}$  lbs., shows Widmanstätten figures and twin-lamellæ (Neumann lines) on the etched surface and consists of blades of kamacite with thin plates of tænite and grains of troilite. Analysis by W. S. Chapman gave:

Fe.	Ni.	Co.	S.	P.	Insol.	Total.	Sp. gr.
88.85	9.07	0.34	0.75	0.27	0.03	99.31	7.693

L. J. S.

**Analysis of the Sulphurous Waters of Vernet-les-Bains.** By LÉON FERRER (*J. Pharm. Chim.*, 1901, [vi], 14, 385—389).—The waters of Vernet-les-Bains belong to the class of thermal sulphuretted alkaline waters. Complete analyses of samples from seven different springs are given in the paper. H. R. LE S.

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### Physiological Chemistry.

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**Artificial Parthenogenesis.** By S. J. HUNTER (*Amer. J. Physiol.*, 1901, 6, 177—180).—The experiments were made on the eggs of *Arbacia*, and show that sea water concentrated by evaporation will produce the formation of imperfect larvæ. This is regarded as confirming Loeb's osmotic theory of artificial parthenogenesis.

W. D. H.

**Influence of Spermatotoxin on Reproduction.** By MDLLE. C. DE LESLIE (*Compt. rend.*, 1901, 133, 544—546).—On injecting into the white male rat spermatotoxic serum from the guinea pig, it loses all



power of reproduction. The sterility lasts for 16—20 days. Sterility may be similarly produced in the female. The injection does not otherwise influence the well being of the animals; the males even continue to produce mobile spermatozoa; these, however, have lost their power of fertilisation.

W. D. H.

**Quantitative Observations on Gastric Digestion.** By FRIEDRICH KRÜGER (*Zeit. Biol.*, 1901, 41, 467—483. Compare Abstr., 1901, ii, 561).—The general belief that the action of pepsin, like that of other enzymes, is inhibited by the presence of digestive products is well founded. The addition of peptone to the mixture lessens the digestive action. Tables are given which show that the inhibitory action of the digestive products is proportional to their quantity, provided the amount of hydrochloric acid is kept constant; in ordinary digestion, this is not the case; the loss of power is greater and is to be in part explained by diminution in the amount of free acid. The amount of free hydrochloric acid which is most favourable is from 0.18 to 0.4 per cent.

W. D. H.

**Blood Analysis in Relation to Metabolism.** By G. ASCOLI (*Pflüger's Archiv*, 1901, 87, 103—115).—It is pointed out that in studying metabolism, the examination of the excreta alone does not teach the details of the metabolic cycle. Intermediate stages, especially in relation to nitrogenous metabolism in the organs, should be searched for, by the examination of the blood for such substances as purine compounds, carbamic acid, creatine, &c.

W. D. H.

**Influence of Sodium Nitrate on Metabolism in Dogs.** By E. ROST (*Chem. Centr.*, 1901, ii, 864; from *Arbb. Kais. Ges.-A.*, 18, 78—99).—Small doses of sodium nitrate have practically no effect on metabolism. Large doses given in water produce diuresis and a 'nitrogen-sparing' action. If insufficient water is given, there is an increase of proteid katabolism. Among different sodium salts, the carbonate produces the greatest increase in the breakdown of proteid material in the body.

W. D. H.

[Proteid Metabolism in Inanition.] By ERWIN VOIT (*Zeit. Biol.*, 1901, 41, 502—549; 550—571).—These two papers are largely critical. The main conclusion arrived at is that proteid katabolism in starvation is largely influenced by the amount of reserve and circulating fat in the body. When the quantity of fat is large, no increase of proteid disintegration occurs, but when it sinks below a certain limit, disintegration begins. Length of life during starvation therefore depends largely on the amount of fat to start with. Death is due, not to destruction of the total cell-masses of the body, but on katabolic changes in a few organs of essential importance.

The second paper deals at greater length with the influence of fat on proteid katabolism.

W. D. H.

**Rôle of Purine Derivatives in Human Metabolism.** By RICHARD BURIAN and HEINRICH SCHUR (*Pflüger's Archiv*, 1901, 87, 239—354. Compare Abstr., 1900, ii, 489).—In birds, uric acid is

the main end-product of nitrogenous metabolism. In mammals, the question is a debatable one whether the uric acid and other purine derivatives which these animals excrete are to be regarded as terminal or intermediate products. A full and critical review of the extensive literature on the subject shows how diverse are the views which are held. The purine derivatives of the urine have a double origin, *exogenous* from the nuclein and purine compounds of the food, and *endogenous* from tissue metabolism. The problem is complicated by the fact that the organism not only forms purine compounds, but it also has the power of destroying them. This property is especially possessed by the liver, so that the excretion of purine compounds is no measure of the amount found unless at the same time the amount destroyed is also known. The relationship between the two processes can be ascertained by the injection of known quantities of purine compounds either into the blood stream or subcutaneously. Such experiments show mainly the fate of exogenous purine, but endogenous purine is apparently acted on in the same way. The result of the experiments shows that uric acid and purine derivatives are in the main intermediate products of metabolism, but that a certain fraction of these intermediate products is excreted as such by the kidneys. This fraction varies in different animals, but in animals of the same class the integration factor (that is, the number by which the urinary purine must be multiplied in order to obtain the total) is very constant; in carnivora it is 20—30, in the rabbit 6, in man 2; that is, in man, half the uric acid formed is excreted in the urine. W. D. H.

**Amount of Fluorine in Teeth and Bones.** By JODLBAUER [with JOSEF BRANDL] (*Zeit. Biol.*, 1901, 41, 487—492).—Hempel's method of estimating fluorine in bone and teeth gives more trustworthy figures than that of Wöhler-Fresenius. W. D. H.

**Compounds of Mercury and Arsenic in the Liver.** By B. SLOWTZOFF (*Beitr. chem. Physiol. Path.*, 1901, 1, 281—288).—When arsenic is given to animals and accumulates in the liver, it unites with the nuclein, and after gastric digestion is found in the precipitate of nuclein. Mercury, on the other hand, unites with the globulin constituents of the cell-protoplasm. W. D. H.

**Composition of the Fat in Young Children.** By F. SIEGERT (*Beitr. chem. Physiol. Path.*, 1901, 1, 183—188).—Langer (Abstr., 1882, 240) originally stated that the amount of solid fatty acids in the subcutaneous fat of new-born children is relatively great, and that with growth oleic acid increases. This statement has not been confirmed by all subsequent observers (Thiemich, Abstr., 1899, ii, 234). In the present research, a large number of observations is recorded; the mean iodine number for new-born children is 43·36; in successive months, the number is 42·5, 46·9, 47·5, 53·2, 45·5, 49·9, 48·9, 54·75, 58·55, until at 12 months it rises to 62·35, the number for the adult being 65. W. D. H.

**Behaviour of Fat during Autolysis of the Liver.** By F. SIEGERT (*Beitr. chem. Physiol. Path.*, 1901, 1, 114—120).—Four

experiments were made with dogs' livers. The amount of ethereal extract and of higher fatty acids was estimated before and after autolysis (from 7 to 9 days, putrefaction being prevented). The amounts of both are practically the same before and after autolysis.

W. D. H.

**Autolysis and Blood-clotting.** By H. CONRADI (*Beitr. chem. Physiol. Path.* 1901, 1, 136—182).—The juices expressed from various animal organs without exception hasten blood-clotting. After autolysis, the same organs yield solutions which hinder blood-clotting. Both substances are soluble in water and precipitable by alcohol, the one which favours coagulation is rendered inert by boiling, is not diffusible, does not filter through a Chamberland filter, and is rendered still more active by calcium chloride. The substance which hinders coagulation is not influenced by heat or by calcium chloride, diffuses readily, and passes partially through a Chamberland filter. The blood itself when kept also gives rise to this substance. It appears to be analogous to peptozyme.

W. D. H.

**Formation of Bactericidal Substances in Autolysis.** By H. CONRADI (*Beitr. chem. Physiol. Path.*, 1901, 1, 193—228).—Bactericidal power is absent from the juices expressed from fresh organs as a rule. It is present in the juice from lymph glands and slightly in that from the spleen. After autolysis, the expressed juice of muscle, liver, spleen, lymph glands, testis, thymus, suprarenal body and duodenum is strongly bactericidal. The juice from bone marrow, ovary, lung, tonsil, kidney, jejunum and ileum has the same power to a less degree. It is absent in the juice after autolysis from foetal intestine, pancreas, thyroid, submaxillary gland, and brain. The bactericidal substances are hydrolytic decomposition products of proteids, and from their reactions and solubilities are probably derived from the aromatic complex of the proteid molecule. They give Millon's, the xanthoproteic, and bromine reactions. They are soluble in alcohol and are precipitated from their alcoholic solutions by ether.

W. D. H.

**Function of Brunner's Glands.** By KARL GLAESSNER (*Beitr. chem. Physiol. Path.*, 1901, 1, 105—113).—The fluid obtained by autolysis of the mucous membrane of the small intestine has certain digestive powers. If a portion is taken which contains both Brunner's and Lieberkühn's glands, the action is both proteolytic and diastatic. If there are only Lieberkühn's follicles, proteolytic power is absent. If the upper part of the duodenum is taken and the surface layer containing Lieberkühn's follicles removed and only Brunner's glands left, the diastatic power is absent. Inverting action on cane sugar, and emulsifying action on fats were absent throughout. The proteolytic enzyme of the Brunner's glands acts in weakly alkaline, neutral, and feebly acid solutions; it is regarded as identical with the enzyme, separated from the pyloric end of the stomach, which the author has named pseudopepsin.

W. D. H.

**Gluco-proteids of Lower Animals.** By OTTO VON FÜRTH (*Beitr. chem. Physiol. Path.*, 1901, 1, 252—258).—The gluco-proteid of the egg

covers of sepia, or of the ground substance of chondrosia were investigated. The reducing substance obtained in each case was an amino-sugar of the type of glucosamine. W. D. H.

**Nucleo-histon.** By IVAR BANG (*Beitr. chem. Physiol. Path.*, 1901, 1, 189—192).—Further reasons are advanced which bear out the author's previous contention that nucleo-histon in the sense of Lilienfeld and Kossel does not exist. W. D. H.

**Formation and Secretion of Chymosin (Rennin).** By ALEXANDER WINOGRADOFF (*Pflüger's Archiv*, 1901, 87, 170—228).—There is an inverse proportion between the quantity of rennet ferment and time of coagulation. A method is described for estimating the amount of the ferment. The ferment is believed to participate in the regeneration of proteid from peptone, and the results obtained by estimating its power of forming plastein are identical with those obtained in experiments on milk. After a meal, the formation of rennin by the gastric mucous membrane increases from the first to the ninth hour; there are two maxima, namely, from the second to the fifth, and from the ninth to the eleventh hour. Even after this time, the ferment is still secreted in small quantities. The amount in the gastric juice is proportional to that in the mucous membrane and very closely follows the curve of pepsin formation. W. D. H.

**Tyrosinase in Animals.** By OTTO VON FÜRTH and HUGO SCHNEIDER (*Beitr. chem. Physiol. Path.*, 1901, 1, 229—242).—Tyrosinase is an enzyme, described by Bertrand as occurring in the juices of certain plants (*Abstr.*, 1896, ii, 571), which oxidises tyrosine and leads to the darkening of the juice. It is apparently analogous to the lac-case of certain other plants. It has been found by Biedermann (*Abstr.*, 1898, ii, 614) in the intestine of the meal worm. The present research shows that it is a constant constituent of the blood of insects and other arthropods, and is the cause of the darkening of the blood on exposure to the air. The chemical nature of the chromogen in the blood is left uncertain; it is, however, not tyrosine. The melanin formed contains C, 55.44; H, 4.45; N, 13.74; it is believed to be related to the indole group, but its chemical nature is also left uncertain. W. D. H.

**Excretion of Uric Acid.** By HELLMUTH ULRICI (*Chem. Centr.*, 1901, ii, 1024—1025; from *Arch. exp. Path. Pharm.*, 46, 321—337).—Sodium benzoate increases the excretion of uric acid. Gallic acid acts in the same way. Quinic acid and tannin have no influence on metabolism or the excretion of uric acid. Salicylic acid produces a great stimulation of metabolic processes, increases the total output of nitrogen, and especially raises that of uric acid; this is followed by a diminution in the excretion of the acid. W. D. H.

**Physiological Action of Chloral Hydrate and Acetone.** By C. ARCHANGELSKY (*Chem. Centr.*, 1901, ii, 1028—1029; from *Arch. exp. Path. Pharm.*, 46, 347—371).—A method of estimating chloral

hydrate in the blood and tissues is described. In dogs, 0·03 to 0·05 per cent. in the blood causes narcosis; 0·05 to 0·07 abolishes the corneal reflex; and 0·11 to 0·12 causes cessation of breathing; in the rabbit, rather larger doses are necessary. In the blood, most of the chloral is present in the corpuscles; at first, the brain contains less than the blood; that in the liver remains small, but the brain tissue which is believed to have a special affinity for chloral hydrate soon contains much more than the blood.

Acetone in the blood to the extent of 0·5 per cent. causes narcosis; it is chiefly present in the corpuscles. The brain contains more, the liver less, than the blood. The central nervous system has also a special affinity for this drug. Both narcotics are believed to be united to the fatty constituents of protoplasm.

W. D. H.

**Acid Poisoning in Dog and Rabbit.** By KARL SPIRO (*Beitr. chem. Physiol. Path.*, 1901, 1, 269—280).—Many previous observers have pointed out that carnivora are less susceptible to the toxic influence of acids than herbivora, and some have attributed this to a fundamental difference between the animals, the carnivora, by production of ammonia, being able to neutralise the acid. It is now pointed out that the difference, although it exists, is only a quantitative one, and that acids and acid phosphates stimulate the kidney to increased activity in the dog more than in the rabbit; the dog thus rapidly eliminates the harmful material. Other diuretics (caffeine and its homologues) also act more powerfully on the dog's kidney than on that of the rabbit; the dog's kidney, moreover, has a higher resistance towards poisonous substances.

W. D. H.

**Condition of the Blood and Marrow in Chronic Arsenical Poisoning.** By I. C. MUIR (*J. Pathol. Bacteriol.*, 1901, 7, 420—446).—In chronic arsenical poisoning in man, the blood is richer in red corpuscles and hæmoglobin when there is deep cutaneous pigmentation than when the skin is but slightly pigmented. Pigmentation is not due to destruction of hæmoglobin, but melanin may be a precursor of hæmoglobin. Arsenic stimulates the erythroblastic action of red marrow, especially when the skin has a store of melanin in it.

W. D. H.

**Behaviour of Calcium Hypophosphite [when administered internally].** By MASSOL and GAMEL (*J. Pharm. Chim.*, 1901, [vi], 14, 337—342).—Contrary to the usually accepted statements, it is definitely shown from the results of experiments carried out on dogs, that when calcium hypophosphite is administered internally, the hypophosphite is not oxidised to phosphate, but is entirely eliminated by the urine as sodium hypophosphite, and that the calcium is eliminated by the fæces. The volume of urine, the total nitrogen, and the amount of urea are not changed, but the acidity of the urine, the amount of uric acid, and the ratio of uric acid to urea are diminished. Complete analyses of the urine, before and after treatment, are given in the original paper.

H. R. LE S.

**Antagonism of Curare and Physostigmine.** By JULIUS C. ROTHBERGER (*Pflüger's Archiv*, 1901, 87, 117—169).—Bilateral antagonism exists between curare and physostigmine so far as their action on muscles is concerned. Those muscles which, like the diaphragm, are last paralysed by curare, are first set free again by the injection of physostigmine. Physostigmine also stimulates the respiratory centre. There is no antagonism between the two drugs *in vitro*.

W. D. H.

**Action of Fluorescent Materials on Ciliated Epithelium.** By RICHARD JACOBSON (*Zeit. Biol.*, 1901, 41, 444—466).—Light increases the poisonous action of fluorescent substances on ciliated epithelium. Non-fluorescent poisonous substances act equally vigorously in light and darkness. Non-poisonous fluorescent substances act in the same way in light and darkness.

W. D. H.

**Chemical Action of the Microsporon Audouini.** By W. D'ESTE EMERY (*J. Pathol. Bacteriol.*, 1901, 7, 400—408).—It has been surmised that the ringworm fungus (*Microsporon audouini*) has the power of digesting keratin. This view is not confirmed. The fungus, however, secretes a proteolytic enzyme which finds its proteid pabulum near the hair bulbs, and the action of which is to set up slight folliculitis; the loss of hair is in part due to this, and in part to splitting caused by mechanical pressure.

W. D. H.

**Phloridzin Diabetes in Cats.** By JULIUS F. ARTEAGA (*Amer. J. Physiol.*, 1901, 6, 173—176).—In the fasting cat, just as in the rabbit and goat, the urinary ratio between dextrose and nitrogen in phloridzin diabetes is 2·8 : 1, a striking example of biological uniformity.

W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Assimilation of Free Nitrogen by Soil Bacteria without Symbiosis with Leguminosæ.** By JULIUS KÜHN (*Bied. Centr.*, 1901, 30, 660—663; from *Fühling's Landw. Zeit.*, 1901, 2).—The results of field experiments on rye during 21 years show that the yields of grain and straw on the unmanured plot and on the plot which has had only non-nitrogenous manures tend to increase rather than diminish. The soil evidently contains fair amounts of available mineral matter, whilst experiments with nitrogenous manure indicate a limited supply of available nitrogen. The conclusion is therefore drawn that fixation of elementary nitrogen is going on under the influence of soil organisms.

Krüger has isolated a micro-organism from the soil, which, in cultivations in artificial solutions, assimilated not inconsiderable amounts of free nitrogen.

The yield of rye on the different plots was as follows (kilos. per hectare):

	1879.		1894—1898.		1899.	
	Grain.	Straw.	Grain.	Straw.	Grain.	Straw.
1. Dung .....	2400	3870	2774	5696	2405	5565
2. Minerals .....	1770	2520	1976	4363	1640	4020
3. „ + ammonium sulphate + nitrate.....	2570	4080	2926	5968	2675	5950
4. Ammonium sulphate + nitrate .....	2560	3570	2664	5224	2370	5030
5. Unmanured .....	1820	2490	1974	3914	1750	3730

The season of 1899 was unfavourable to grain production.

N. H. J. M.

**Decomposition of Nitrates and Nitrites by Bacteria.** By ALBERT MAASSEN (*Chem. Centr.*, 1901, ii, 820—821; from *Arb. k. Ges.-A.*, 18, 1—77).—Potassium nitrate in 0.5 per cent. solutions containing peptone (5 per cent.) was reduced to nitrite by 85 of the 109 varieties of microbes examined. Fifty varieties destroyed nitrites, four of them liberating free nitrogen. Many bacteria which reduced nitrites, without liberation of nitrogen, had very little or no effect on nitrates. The presence of carbohydrates is favourable to denitrification, whilst in absence of organic nitrogen, nitrates and nitrites are attacked by microbes which have no effect when proteids are present.

The so-called denitrifying organisms destroy nitrates independently of the nature of the nutritive solutions, whilst the others act only in presence of certain carbon compounds. The action of both classes of microbes is retarded by the presence of highly oxygenated compounds, such as chlorates, without injury to their growth.

Some bacteria, such as *Bacterium praepollens*, act on nitrates only in symbiosis with other varieties, liberating nitrogen and producing potassium carbonate. The co-operating bacteria, in the case of *B. praepollens*, are exclusively those which reduce nitrates to nitrites.

N. H. J. M.

**Decompositions of Nitrogen Compounds in Soil by Lower Organisms.** By W. KRÜGER and W. SCHNEIDEWIND (*Chem. Centr.*, 1901, ii, 824—825; from *Landw. Jahrb.*, 30, 633—648. Compare *Abstr.*, 1901, ii, 470).—Application of straw, in field experiments, resulted in a lessened assimilation of nitrogen and a diminished crop. The injurious effect of fresh organic matter on the assimilation of nitrogen by the crop is to a great extent due to production of insoluble nitrogenous compounds, under the influence of denitrifying and other microbes and fungi. The nitrogen not only of nitrates but especially of ammonium salts and amides becomes unavailable. The insoluble nitrogen becomes available only slowly; most of it, perhaps, not at all.

Ammonium sulphate (but not nitric nitrogen) is partly converted into proteids even in absence of fresh organic manure. This explains why ammonium salts supply less nitrogen to crops than nitrates when the latter are not subjected to loss by drainage.

N. H. J. M.



**Effect of Methylal on some Fresh-water Algæ.** By **RAOUL BOUILHAC** (*Compt. rend.*, 1901, 133, 751—753).—*Nostoc* and *Anabaena* are able to grow in presence of methylal when the amount of light is insufficient for the decomposition of carbon dioxide; in absence of methylal or other organic matter, there is no growth under these conditions. A certain amount of light is necessary when methylal is present.

Experiments are proposed to ascertain whether methyl alcohol and formaldehyde respectively can replace methylal. N. H. J. M.

**Constituents of Coffee Berries.** By **L. GRAF** (*Zeit. angew. Chem.*, 1901, 14, 1077—1082).—Coffee berries do not contain dextrose or any reducing sugars in the free state. The presence of sucrose in the methyl alcoholic extract has been established. It appears that sucrose after crystallisation from methyl alcohol melts at 169—170°, but after crystallisation from ethyl alcohol at 179—180°.

Caffetannic acid is also a constituent of coffee beans; although generally regarded as a glucoside, it does not yield a sugar on treatment with dilute acids, concentrated alkali, bromine or dilute nitric acid (compare Kunz-Krause, *Abstr.*, 1893, ii, 327; 1897, i, 530; F. Koch, *ibid.*, 1895, ii, 410; Hlasiwetz, *Annalen*, 1867, 142, 219; Cazeneuve and Haddon, *Abstr.*, 1897, i, 529). J. J. S.

**Presence of Salicylic Acid in Strawberries. Errors of Analysis which may result therefrom.** By **L. PORTES** and **A. DESMOULIÈRES** (*J. Pharm. Chim.*, 1901, [vi], 14, 342—351).—Salicylic acid has been actually isolated from ten different varieties of strawberries, and is shown to be a normal constituent of this fruit. The acid is most probably present as methyl salicylate. The amount present, although small, 1 mg. having been obtained from 1 kilogram of the fruit, is sufficient to answer to the reactions employed for the detection of salicylic acid in cases of suspected adulteration. H. R. LE S.

**Formation of the Perfume of Vanilla.** By **HENRI LECOMTE** (*Compt. rend.* 1901, 133, 745—748).—The fruit of *Vanilla planifolia* does not possess the characteristic odour of vanilla at the period of cropping; the odour is developed during the process to which the fruit is subsequently subjected. Evidence is adduced in support of the view that vanillin is formed by the action of a ferment on coniferin, the coniferyl alcohol thus produced being transformed by an oxydase into vanillin.

Oxydase was found in the best preparations of vanilla (from Mexico, Reunion, Mayotte, and Seychelles), but was absent, or nearly so, in inferior preparations from Tahiti and in "vanillon" from Guadeloupe. All the materials examined contained manganese. N. H. J. M.

**Production of Milk and Butter. Variations in the Richness of Milk in Fat.** By **L. MALPEAUX** and **E. DOREZ** (*Ann. Agron.*, 1901, 27, 449—461).—The minimum and maximum amounts of different constituents found in milk were as follows:—water, 84·5—89·6; fat, 10·4—15·5; casein, 2·9—3·8; lactose, 4·6—5·4; ash,

0.6—0.9 per cent. A low percentage of fat is not necessarily coincident with a large yield of milk. The last portion of the milk obtained in milking was found to be much richer in fat than the first portion, but contained somewhat less of the other constituents.

Soon after calving, the amount of fat is above the average, but subsequently there is a regular decrease, which, in some cases, may be considerable.

N. H. J. M.

**Poisoning by Potassium Perchlorate.** By F. R. JUNGNER (*Bied. Centr.*, 1901, 30, 711; from *Deut. landw. Presse*, 1900, No. 62).—Germination experiments were made with rye both with and without sodium nitrate (1 gram, corresponding with the amount usually applied per acre). In presence of perchlorate eight different symptoms of injury were observed, and there were also differences in composition.

N. H. J. M.

**Effect of Various Mechanical Conditions of the same Soil on Barley.** By JOHANN J. VANHA (*Bied. Centr.* 1901, 30, 654—657; from *Zeit. Landw. Versuchs-Wes. Oesterr.*, 1901, 4, 99).—Barley was grown in pots containing loamy clay soil, and the same soil to which varying amounts of sand and of silt respectively had been added. The same manures and the same amount of water were added to each pot.

As the fineness of the soil increased there was an increase in the yield of grain and straw; the number, length, and weight of the ears and the weight of the grain were also increased. Light sandy soil favoured the production of mealy grain, and the grain is smaller and accumulates more ash constituents than in heavy soil. The amounts of nitrogen and ash in the grain produced in the normal soil (1), and in the soil with  $\frac{3}{4}$  sand (2), and with  $\frac{1}{2}$  silt (3), were as follow:—N (1) 1.667, (2) 1.830, and (3) 1.575. Ash, (1) 2.600, (2) 2.740, and (3) 2.432 per cent.

In the original paper, fifty different properties of the single plants are discussed. Analyses of the ears and the grain are given.

N. H. J. M.

**Assimilation by Oats with different Amounts of Moisture in the Soil and with different Manures.** By L. LANGER and BERNHARD TOLLENS (*J. Landw.*, 1901, 49, 209—229).—An increase in the amount of water in the soil gave rise to increased production of grain and straw; at the same time, the percentage amount of phosphoric acid and also that of potassium (when the soil contained plenty of potassium, but not otherwise) in the produce were raised. The percentage amount of nitrogen in grain and straw diminished as the amount of soil moisture increased.

Root production diminished when the amount of water in the soil was increased, and *vice versa*.

Exclusive phosphoric acid manuring increased the total produce in soils deficient in nitrogen when the soil moisture was increased. The produce contained the greatest amount of phosphoric acid when grown on soil poor in phosphoric acid.

Excess of potassium manure in conjunction with much water promoted the growth of straw, but diminished the yield of grain.

Heinrich's results, indicating that the roots show deficiency of manures in the soil, are generally confirmed; but minimum numbers have to be modified according to the amount of water.

Langer, in opposition to Tollens, considers that the results of the analysis of oats give indications as good as, or better than, soil analysis as to the manurial constituents of the soil (compare Atterberg, *Abstr.*, 1901, ii, 573).

N. H. J. M.

**Manurial Experiments with Beans and Barley on Heavy Marsh Soil.** By LILIENTHAL (*Bied. Centr.*, 1901, 30, 666—668; from *Fühling's Landw. Zeit.*, 1901, 80).—Field experiments with beans followed by barley on limed and unlimed plots, without manure, and with basic slag, guano, and a mixture of basic slag, sodium nitrate, and kainite respectively.

It was found that lime neutralises to a great extent the injurious effect of salts on heavy marsh land and that the amount of lime present in basic slag is not sufficient to obtain the greatest yields. When liming is adopted for rich marsh land, manures must at first be applied with caution, especially for cereals, to avoid the crop being laid.

Horse beans do not require nitrogenous manure on marsh land; fixation of nitrogen increases with the supply of phosphoric acid in the soil.

The phosphoric acid of basic slag is more effective on marsh land than that of crude guano.

N. H. J. M.

**Sweet Potato.** By LOUIS BONNIN (*Ann. Agron.*, 1901, 27, 491—492; from *Bull. Assoc. Chim. suc. dist.*, 1901, 1028).—The following analyses are given of (1) the meal obtained by grinding the sun-dried tubers of *Ipomœa batatas*, (2) the creepers, and (3) the residues obtained after extracting the starch (13—14 per cent.) from the meal:

	Water.	Fat.	Nitrogenous. matter.	Non-nitrog. matter.	Cellulose.	Ash.
(1)	11.40	1.96	3.06	78.77	2.69	3.12
(2)	84.51	0.56	2.03	8.16	2.47	1.37
(3)	24.86	0.48	0.55	69.49	3.82	0.80

The meal and the extracted meal form suitable cattle foods when mixed with molasses, whilst the creepers are used for cows.

N. H. J. M.

**Conditions of Temperature and Moisture of a Loamy Soil with different Crops and different Manures.** By CONRAD VON SEELHORST (*J. Landw.*, 1901, 49, 231—250).—The result of pot experiments showed that the unmanured soil gave up the most water and the soils which received potassium manure and sodium nitrate, or a mixture of both, the least water. Superphosphate had not much effect. The pot with potassium manure and superphosphate lost

water more quickly than the superphosphate pot, whilst potassium carbonate alone strongly retained water.

In subsequent experiments with sand, it was again found that the evaporation was greatest without manure or with superphosphate. Calcium carbonate had practically no effect.

A large number of moisture determinations were made in soils growing different crops and with different manures. The soil of plots which received no nitrogen always contained the greatest amounts of water owing to the increased evaporation from the crop. The difference in the amount of moisture exists long after the removal of the crop.

Manuring has only an indirect influence on the temperature of the soil, due to the greater amount of shade by denser crops. The differences, however, do not seem to be of practical importance.

N. H. J. M.

**Relative Manurial Value of Ammonium Salts [and Sodium Nitrate].** By PAUL WAGNER (*Bied. Centr.*, 1901, 30, 668—670; from *Mitt. deut. landw. Ges.*, 1901, Nos. 10 and 11).—The results of field experiments in 1899 and 1900 in which rye, oats, barley, sugar beet, mangels, and potatoes were manured with sodium nitrate and ammonium salts respectively, showed the relative value of the two forms of nitrogen to be as 101 : 67 for grain and as 100 : 65 for straw, in the case of the three cereals taken together. The season was, however, in both years, unfavourable for the utilisation of ammonium salts.

In the case of roots, the value of the ammoniacal nitrogen was only 48 as compared with nitric nitrogen = 100. This is, perhaps, to be partly attributed to the action of the sodium of the nitrate.

None of the soils on which the experiments were made were, physically, exceptionally unfavourable for ammonium salts; but it is possible that some, even those richer in calcium, contained too little calcium carbonate for the rapid conversion of ammonia into nitrate.

N. H. J. N.

**Manurial Experiments with Sodium Nitrate in the Redwine District of Ahrthal.** By PAUL KULISCH (*Bied. Centr.*, 1901, 30, 670—671; from *Ber. k. Lehranstalt Obst-, Wein-, u. Gartenbau, Geisenheim a. Rhein*, 1900, 103).—The application of sodium nitrate (300 kilos. per hectare) had a very striking effect on the stony, hilly land; more stem and leaf were produced, whilst the development of the grapes was improved. In the case of humous loam, nitrate had very little effect.

Sodium nitrate had no injurious effect on the must. Any differences which were observed were in favour of the manured plots.

N. H. J. M.

**Employment of Ammoniacal Manures on Calcareous Soils.** By ERCOLE GIUSTINIANI (*Ann. Agron.*, 1901, 27, 462—486. Compare *Abstr.*, 1899, ii, 692).—Ammonium manures may be used with advantage on damp, and generally on stony, soils containing calcium

carbonate. In rich soils, nitrification is slow, and the effect of ammonium salts is less rapid, but more durable, than that of sodium nitrate. Ammonium salts should not be applied to sandy soils which contain no calcium carbonate, or to sandy, calcareous soils. A light soil, with 5—20 per cent. of calcium carbonate, may, if not too dry, benefit by application of ammoniacal manures; the manure might, with advantage, be added by degrees.

When basic slag and ammonium sulphate are employed for the same soil, the former should be applied some days in advance in order to convert the free lime into carbonate.

N. H. J. M.

### Solubility of Phosphatic Manures in some Organic Acids.

By WALTER F. SUTHERST (*Chem. News*, 1901, 84, 199—200).—A gram of the phosphate and a gram of citric acid, or a quantity of acetic or tartaric acid to give the same total acidity, were made up to 100 c.c. with water, left in contact for 24 hours with frequent agitation, then filtered, and the phosphoric acid estimated in the solution with the following results per cent., calculated as tricalcium phosphate.

	Acetic acid.	Tartaric acid.	Citric acid.
Coprolite.....	10·13	32·60	17·17
Basic slag .....	12·30	15·85	19·67
Basic superphosphate.....	18·53	28·37	24·79
Precipitated phosphate ...	43·72	78·12	71·27

The phosphates contained respectively 84·29, 29·13, 28·38, and 80·73 per cent. of phosphoric acid calculated as tricalcium phosphate.

D. A. L.

**Manurial Experiments.** By JOHN SEBELIEN (*Bied. Centr.*, 1901, 30, 671—681; from *Norsk. Landm.-bl.*, 1901, Nos. 12, 13, and 14).—Excessive amounts of artificial manures (more than 10,000 kilos. of kainite per hectare) proved to be very injurious to peas, whilst more than 5000 kilos. of potassium sulphate were beneficial. In the case of carrots, the large amount of kainite was not injurious, but slightly increased the yield (5·9 per cent.), whilst potassium phosphate increased the yield by 32 per cent. The injurious effect of the kainite on peas lasted over the second year when the kainite was applied alone; in the case of the plot which received an excessive amount of superphosphate in addition to the kainite, there was no injury the second year.

The results of pot experiments in which ammonium sulphate and sodium nitrate were compared showed no marked difference, except in absence of potassium, in which case the nitrate gave the greatest yield of barley straw and grain.

Similar experiments with potassium chloride and sulphate showed that the chloride raised the yield of grain, whilst the sulphate increased the yield of straw.

N. H. J. M.

**[Manurial] Action of various Calcium and Magnesium Compounds.** By DIEDRICH MEYER (*Chem. Centr.*, 1901, ii, 825; from *Landw. Jahrb.*, 30, 619—631).—In pot experiments, it was found

that with a mixture of *Lolium perenne* and lucerne and oats, addition of more than 1 gram of calcium oxide in the form of gypsum considerably diminished the yield. Potatoes were not affected by gypsum. Addition of calcium or magnesium carbonate prevented any injurious action by gypsum; addition of soil to the sand also reduced the injurious effect to a minimum, so that there can be no objection, in practice, to the relatively small amounts of gypsum which are employed.

Small amounts of magnesium carbonate increased the yield of *Lolium* and lucerne, whilst large amounts were injurious; horse beans and vetches were not injured by large quantities. Calcium carbonate may be almost completely replaced by magnesium carbonate, but a mixture of the two gives the best results, even when an excess of lime is present. Dolomite marl is therefore at least as suitable as pure lime marl.

N. H. J. M.

**Drainage Water.** By CREYDT, CONRAD VON SEELHORST, and WILMS (*J. Landw.*, 1901, 49, 251—275).—The field from which the drainage was collected had an area of 4·81 hectares. The cropping had been as follows: 1897, roots; 1898, wheat; 1899, beans, and 1900, roots. The manures applied were ammonium sulphate, sodium nitrate, and superphosphate. The daily amounts of rainfall and the estimated amounts of drainage from July, 1899, to August, 1900, are given in tables. Analyses were made in a large number of mixed samples of the drainage.

It was found that in winter there was more drainage than rain, and the constituents of the winter drainage were therefore not derived from the surface of the field alone.

The maximum and minimum amounts of the different substances found in the drainage were as follows:  $K_2O$ , 1·75—3·69;  $CaO$ , 157·0—184·0;  $MgO$ , 31·3—46·4;  $SO_3$ , 43·5—59·2; and  $N_2O_5$ , 1·0—8·2 per million. Increased temperature seemed to increase the amount of lime, owing to greater production of carbon dioxide. Traces of phosphoric acid were always present in the drainage.

The estimated losses per hectare are as follows:  $K_2O$ , 8·4;  $CaO$ , 630;  $MgO$ , 140;  $SO_3$ , 182; and  $N$ , 4·4 kilos. The loss of potassium is very slight, whilst that of phosphoric acid is still less.

N. H. J. M.

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### Analytical Chemistry.

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Microchemical Test for Alkalis and Acids; Detection of small Quantities of Ozone and Water. By FRIEDRICH EMICH (*Monatsh.*, 1901, 22, 670—678).—As a microchemical test for alkalis and acids, the author uses silk dyed either with red or blue litmus. A drop (0.05 mg.) of the liquid the reaction of which is to be tested is placed on a glass slide and observed under a microscope magnifying

200 times, a condenser being used. Into this drop, a silk thread coloured with litmus is introduced. It is found that a perceptible colour change is given by the following quantities of alkalis, stated as millionths of a milligram; 0.3 of sodium or potassium hydroxide, lithium, or caesium carbonate; 0.5 of sodium, potassium, or rubidium carbonate; 30 of barium hydroxide and 10 of calcium hydroxide; and of acids 0.5 of sulphuric, hydrochloric, or nitric acid; 1 of oxalic and 3 of acetic acid. Solutions of lithium, potassium, or rubidium carbonate, which have no effect on the colour of the flame, will yet give a marked reaction with the above reagent.

Silk coloured with litmus can also be used for the detection of ozone, in the presence of potassium iodide or potassium ferrocyanide when red litmus is used, or of sulphur or potassium thiocyanate with blue litmus.

K. J. P. O.

**Methods of Standardising Acid Solutions.** By CYRIL G. HOPKINS (*J. Amer. Chem. Soc.*, 1901, 23, 727—740).—The author has studied the respective merits of the following methods for standardising volumetric acids: the silver chloride method, conversion into ammonium sulphate, use of metallic sodium, use of pure crystallised borax, electrolysis of copper sulphate, and standardising oxalic acid by means of metallic iron and potassium permanganate. Of these, the first two methods gave the best results.

In the silver chloride method, a carefully measured quantity of approximately correct hydrochloric acid is precipitated with silver nitrate and the resulting silver chloride is collected in a Gooch crucible, washed, dried at 130—150°, and weighed. The ammonium sulphate method consists in neutralising a definite volume of approximately correct sulphuric acid with ammonia and drying the residue at 120° (compare Weinig, *Abstr.*, 1893, ii, 245).

L. DE K.

**Normal Alkalis and Indicators in Acidimetry.** By C. A. JUNGCLAUSSEN (*Chem. Centr.*, 1901, ii, 896—897; from *Apoth. Zeit.*, 16, 664—666).—Normal potassium hydroxide may be conveniently made from fresh ordinary “caustic potash purified by alcohol.” The solution should then be standardised with normal hydrochloric or oxalic acid, phenolphthalein being used as indicator. Although the solution may not be free from carbon dioxide, this does not matter in the least whether titrating from acidity to alkalinity or the reverse way, provided the liquid is cold and that phenolphthalein is employed.

A deci- or centi-normal solution may be prepared from the above normal solution and used for the titration from acid to alkaline reaction only, using iodeosin as indicator; the solutions should, however, be checked with  $N/10$  or  $N/100$  hydrochloric acid and the necessary correction applied.

In cases where hæmatoxylin is used as indicator, the alkali should be completely freed from carbon dioxide by cautious addition of barium hydroxide.

L. DE K.

**Estimation of Chlorine in Natural Waters.** By LUDWIG W. WINKLER (*Zeit. anal. Chem.*, 1901, 40, 596—600).—In titrating chlorides by Mohr’s method, the results are seriously too high when



the chlorine present is less than 25 mg. per litre, because a certain amount of silver nitrate is needed to produce a visible precipitate of silver chromate. Using a silver nitrate solution, of which 1 c.c. equals 0.001 gram of chlorine, the amount to be subtracted, when working in the manner here prescribed, is shown in the following table :

Solution used, c.c.....	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	2.0
Correction, c.c. ....	0.2	0.25	0.3	0.33	0.36	0.38	0.39	0.40	0.41	0.44

From 2 c.c. up to 10 c.c., the correction increases regularly by 0.02 c.c. for each additional c.c. of solution used.

In each of two bottles of 150 c.c. capacity, there is placed 1 c.c. of a 1 per cent. solution of potassium chromate. To the first bottle is added about 90 c.c. of the water to be titrated and just enough silver solution to produce a red colour, which is then removed by another 10 c.c. of the water. This mixture then serves as a standard for comparison. To the second bottle, 100 c.c. of the water are added and then silver nitrate until a just visible red colour persists for 5—10 minutes. The bottles must be protected from light as much as possible. The results of some titrations of very weak chloride solutions show that even when the correction is three times the amount to be estimated, very close agreement with gravimetric determinations can be obtained.

M. J. S.

**Estimation of Sulphur and Phosphorus in Iron and Steel.**  
By UBALDO ANTONY (*Gazzetta*, 1901, 31, ii, 274—277).—To rapidly determine sulphur and phosphorus in iron, the author recommends the use of an oxidising mixture consisting of 4 parts of manganese dioxide, 1 of potassium permanganate, and 2 of dry sodium carbonate, the procedure being as follows : 5 grams of the finely powdered sample are well mixed in a platinum crucible with 40 grams of this oxidising mixture, a layer of the latter being also laid on the surface and the whole heated gradually at first, afterwards more strongly, and finally to a bright red heat by means of a blowpipe flame, the mass being meanwhile kept well stirred with a platinum wire. When cool, it is extracted with boiling water, the filtrate acidified with nitric acid and evaporated to a volume of about 30 c.c., to which is added a little ferric chloride, then ammonium chloride and ammonia, the liquid being then heated and filtered ; by this means, silica, phosphates, and arsenates are removed. The filtrate is used for the estimation of the sulphur as barium sulphate, whilst the precipitate is dissolved in hydrochloric acid, the solution evaporated to dryness, and the residue maintained for some time at 120—130°, to insure the insolubility of the silica. The mass is then dissolved in dilute hydrochloric acid and any arsenic removed by means of hydrogen sulphide, the excess of which is then boiled off. Ammonium molybdate is then added to precipitate the phosphoric acid, which is afterwards reprecipitated as ammonium magnesium phosphate and weighed as magnesium pyrophosphate. Other elements, such as tungsten, chromium, &c., often present in steel, can also be detected and determined by this method.

T. H. P.

**New Nitrometer for use with the Sprengel Pump.** By GIUSEPPE ODDO (*Gazzetta*, 1901, 31, ii, 215—217).—This nitrometer, which is especially adapted for collecting and measuring nitrogen in its estimation in organic compounds, is a modification of Schiff's and is fitted near the bottom with three apertures, one for running off the mercury, the second for connecting with the Sprengel pump, and the last, which is slightly above the other two, for the entry of the potash solution. A sketch of the apparatus is given. T. H. P.

**Action of Ammonium Carbonate on the Arsenic Sulphides** By LUDWIG VANINO and C. GRIEBEL (*Zeit. anal. Chem.*, 1901, 40, 589—591).—Solutions of arsenious or arsenic sulphide in ammonium carbonate should, when acidified, yield in the form of sulphide the whole of the arsenic they contain, without the necessity for adding hydrogen sulphide. Practically, however, some hydrogen sulphide is always given off on adding acid, and the precipitation is consequently incomplete. If, however, the solution is largely diluted and acidified in a bottle, which is then closed for 24 hours, the hydrogen sulphide is re-absorbed and every trace of arsenic is precipitated. If an open vessel is used, or a concentrated solution is acidified, addition of hydrogen sulphide is indispensable.

In separating the arsenic sulphides from those of tin and antimony by concentrated hydrochloric acid, boiling must be avoided, or a loss of arsenic by volatilisation will occur. M. J. S.

**Gravimetric Estimation of Boric Acid.** By ALFRED PARTHEIL and J. A. ROSE (*Ber.*, 1901, 34, 3611—3612).—The distribution ratio obtained by shaking *N*/10 boric acid solution with ether at 26° is 34.2 : 1. The boric acid solution, acidified with hydrochloric acid, is extracted with ether for some 18 hours in a specially constructed extractor or 'perforator,' in which the ether is made to work its way continually through the aqueous solution contained in a spiral tube. The flask containing the ethereal solution is afterwards placed in a vacuum desiccator over sulphuric acid and the residue weighed. The ether must not be distilled off at the atmospheric pressure, as boric acid volatilises with ether vapour. The method gives good results and may be employed for estimating the acid in various minerals. Sulphuric, phosphoric, and nitric acids, or appreciable amounts of iron, must not be present. J. J. S.

**Separation and Estimation of small amounts of Potassium in Saline Mixtures.** By FREDERIK H. VAN LEENT (*Zeit. anal. Chem.*, 1901, 40, 569—573).—From solutions containing small amounts of potassium with large quantities of sodium chloride, magnesium and calcium salts, the potassium is best separated as potassium cobaltinitrite, after which it may be weighed as perchlorate or platinichloride. The calcium and most of the magnesium should be removed by sodium carbonate. The filtrate is then slightly acidified with acetic acid and treated with the cobalt reagent, which is prepared by mixing, just before use, equal volumes of sodium nitrite solution (180 grams per litre) and cobalt solution containing 19.16 grams of crystallised cobalt

chloride, and 50 c.c. of glacial acetic acid in a litre. The precipitate is allowed to subside for 6—7 hours at 40—50°, and then all night in the cold, and after collecting on a filter is washed once with the reagent and then thoroughly with 80 per cent. alcohol. The dried precipitate is decomposed by evaporating with hydrochloric acid; perchloric acid is then added, and the mixture evaporated until white fumes are given off. The potassium perchlorate is triturated and washed with 96 per cent. alcohol, to which 0.2 per cent. of perchloric acid has been added, and then on the filter with ether-alcohol. It is dried on the filter at 120—130° and weighed. For weighing as platinichloride, the yellow precipitate should be decomposed by gentle ignition, the potassium nitrite dissolved out by a weak sodium chloride solution (to prevent the cobalt oxide from passing through the filter), and evaporated with hydrochloric acid to convert it into potassium chloride.

M. J. S.

**Estimation of Hydroxide in the Presence of Alkali Carbonate.** By W. E. RIDENOUR (*Chem. News*, 1901, 84, 202).—The author has tested the process of titration of alkali hydroxide in the presence of carbonate, using first phenolphthalein and then methyl-orange; he finds that phenolphthalein does not indicate half the carbonate, either alone or in presence of the hydroxide. To ascertain the number of c.c. of normal acid corresponding with the carbonate in a mixture of alkali hydroxide and carbonate he multiplies by 2 the number of c.c. of normal acid indicated by methyl-orange, using phenolphthalein, then methyl-orange, and divides by 104.5726. D. A. L.

**Estimation of Cadmium.** By EDMUND H. MILLER and ROBERT W. PAGE (*Zeit. anorg. Chem.*, 1901, 28, 233—241).—The electrolytic method of estimating cadmium is convenient and gives trustworthy results if care is taken to avoid a large excess of potassium cyanide and the presence of other salts. A current of 0.1 to 0.15 ampere is employed and the estimation takes about 16 hours.

The estimation by precipitation with sodium carbonate gives very unsatisfactory results.

A convenient and accurate method is to precipitate the cold neutral cadmium solution with an excess of diammonium phosphate. The precipitate must be allowed to remain for some time and is then transferred to a weighed filter and dried at 105°, or is converted into pyrophosphate and then weighed. The solution must not be heated, since the precipitate of ammonium cadmium phosphate gives off ammonia on boiling and is partially converted into cadmium orthophosphate.

E. C. R.

**Estimation of Mercury in Antiseptic Solutions containing Mercuric Chloride, Iodide, or Cyanide.** By G. MEILLÈRE (*J. Pharm. Chim.*, 1901, [vi], 14, 356—359).—Attention is drawn to the fact that mercurial antiseptic solutions contain, as a rule, other substances besides the mercury salt, so that mere evaporation of the solution and weighing the residue gives erroneous results. With solutions containing mercuric chloride or iodide, accurate results may be obtained by extracting them with ethyl acetate and weighing the residue

left on evaporation of the ethereal solution. Mercuric cyanide may be estimated by means of a standard solution of iodine in the presence of an excess of an alkali hydrogen carbonate. It is necessary to add an excess of the iodine solution, which excess may be estimated by means of a standard solution of sodium thiosulphate. H. R. LE S.

**Gravimetric and Volumetric Estimation of Mercury, Copper, and Zinc.** By ROBERT COHN (*Ber.*, 1901, **34**, 3502—3508).—*Volumetric estimation of mercury.*—An excess of *N*/10 ammonium thiocyanate is added to the solution of mercury and the excess determined after the addition of nitric acid and ferric alum by means of *N*/10 silver nitrate; it is best in the titration to add more silver nitrate than is necessary for decolorisation, and to titrate back with the thiocyanate as in Volhard's method. The method depends on the formation of sparingly soluble, non-dissociating mercury thiocyanate,  $\text{Hg}(\text{CNS})_2$ .

*Volumetric estimation of copper and zinc.*—A solution of mercuric chloride (0.1 mol.) and ammonium thiocyanate (0.4 mol.) in water (1 litre) is standardised by means of *N*/10 silver nitrate according to Volhard's method; on adding to an excess of this a known volume of the copper or zinc solution, a precipitate of the type  $\text{M}''\text{Hg}(\text{SCN})_4$  is formed, and, after filtering, an aliquot portion of the liquid is titrated against the silver nitrate solution. From the difference in the values for the titration of the same quantity of mercuric thiocyanate solution before and after precipitation, the amount of copper or zinc follows from the relationship  $\text{Cu}(\text{or Zn}) : \text{SCN} = 1 : 2$ . The equations involved are, for example, (1)  $\text{HgCl}_2 + 4\text{NH}_4\text{SCN} + 4\text{AgNO}_3 = \text{Hg}(\text{SCN})_2 + 2\text{AgSCN} + 2\text{AgCl} + 4\text{NH}_4\text{NO}_3$ ; (2)  $\text{HgCl}_2 + 4\text{NH}_4\text{SCN} + \text{CuSO}_4 + 2\text{AgNO}_3 = \text{Hg}(\text{SCN})_2 + \text{Cu}(\text{SCN})_2 + 2\text{AgCl} + \text{K}_2\text{SO}_4 + 2\text{NH}_4\text{NO}_3$ .

*Gravimetric estimation of the three metals.*—In the case of copper and of zinc, the precipitate of the type  $\text{M}''\text{Hg}(\text{SCN})_4$  is left for two hours in the cold, filtered, and ignited; with copper, the filter paper and precipitate are burned together, and when a large quantity has to be weighed, the product is converted into cuprous sulphide by reduction in a stream of hydrogen and the addition of sulphur. With smaller amounts, the product is ignited with pure mercuric oxide, and weighed as copper oxide. In the case of zinc, the procedure is similar, but the filter paper has to be initially removed. To estimate mercury, it is precipitated by a solution of zinc sulphate (1 mol.) and alkali thiocyanate (4 mols.), and the zinc oxide, ultimately obtained, weighed. W. A. D.

**Volumetric Estimation of Manganese.** By HUGH RAMAGE (*Chem. News*, 1901, **84**, 209—210).—To correct for various incidental reactions, the method for titrating manganese described by the author and Reddrop (*Trans.*, 1895, **47**, 268) has been modified so far as wrought iron, steel, and pig-iron are concerned:—1.1 gram of the sample is dissolved by boiling with 30 c.c. of dilute nitric acid, the solution is cooled, then boiled for 3 minutes with 0.5 gram, or more, of sodium bismuthate, cooled again, treated with a slight excess of sulphurous acid, reoxidised with 1.5 gram of sodium bismuthate, and filtered. Hydrogen peroxide is run in at first until the reddish colour gives

place to a clear yellow solution, then 0.6 to 1.0 in excess is added. The solution is titrated with *N*/10 permanganate. D. A. L.

**Detection of Chromic Acid by Hydrogen Peroxide in presence of Vanadic Acid.** By C. REICHARD (*Zeit. anal. Chem.*, 1901, 40, 577—586).—The blue colour attributed to perchromic acid, produced by the action of hydrogen peroxide on chromic acid, is destroyed or prevented by the addition of vanadic acid with production of a brown colour. The blue ethereal solution of perchromic acid is decolorised by ammonium metavanadate. Addition of sodium phosphate or arsenate annuls the action of vanadic acid; a nitrate has no such effect. Molybdates and tungstates also destroy perchromic acid, but not so energetically as vanadates. M. J. S.

**Estimation of Uranium.** By EDWARD F. KERN (*J. Amer. Chem. Soc.*, 1901, 23, 685—726).—Uranium solutions may be freed from the metals of the fifth or sixth group by a current of hydrogen sulphide providing 50 parts of the liquid contain no more than 1 part of free hydrochloric or nitric acid. From metals of the third or fourth group, it may be isolated by boiling for 15 minutes with a large excess of sodium carbonate. Ferric iron may be completely separated from uranium by shaking the hydrochloric acid solution three times in succession with pure ether; it is, however, essential that the acid should have a sp. gr. of 1.1 and that the ether be previously saturated with the acid. From an acetic acid solution containing alkalis or alkaline earths, uranium may be precipitated as hydrated oxide,  $U_3O_4 \cdot 3H_2O$ , by electrolysis, or it may be separated by a thrice repeated precipitation in a hot solution with ammonia in the presence of ammonium chloride; the ammonium uranate, at first slimy and yellow, becomes darker and crystalline after 20 minutes' boiling and is readily converted into  $U_3O_8$  by ignition over the blast with free access of air. Uranium may be also separated from alkalis by precipitating the boiling liquid with ammonium phosphate in the presence of ammonium acetate. After boiling for 15 minutes, the precipitate becomes crystalline, and, like the ammonium uranate, it is washed with a 2.5 per cent. solution of ammonium chloride and then ignited in a porcelain crucible. It is then moistened with nitric acid, reignited, and weighed as uranyl pyrophosphate. Several methods are given for the separation of uranium from phosphoric acid, the most convenient process being the treatment of the nitric acid solution with metallic tin at the boiling temperature. The most rapid estimation of uranium is accomplished by reducing the sulphuric acid solution with metallic zinc and titrating the resulting uranous sulphate with standard permanganate in an atmosphere of carbon dioxide. Full particulars will be found in the original paper. Reduction of a hydrochloric acid solution either by zinc or stannous chloride gives unsatisfactory results.

The assay of uraninite (pitchblende) is best made by the ether method, which is briefly as follows: The mineral is dissolved in nitric acid and repeatedly evaporated with addition of hydrochloric acid. After removing lead, copper, &c., by hydrogen sulphide, the filtrate is

boiled and oxidised with nitric acid and precipitated whilst boiling with ammonia. The precipitate which also contains ammonium uranate, is, after washing, dissolved in hydrochloric acid and agitated with ether to remove the ferric chloride. The aqueous acid solution is nearly neutralised with ammonia and then boiled with a large excess of ammonium carbonate. The filtrate which contains the uranium is then boiled down to a small bulk, the precipitate redissolved by addition of hydrochloric acid, and the solution again boiled to expel carbon dioxide. The uranium is then precipitated as directed by ammonia, or by ammonium phosphate, or estimated volumetrically after expelling the chlorine by means of sulphuric acid, or precipitated by electrolysis.

Some ores of uranium such as carnotite contain vanadium. This may be got rid of by simply evaporating the nitric acid solution to dryness, and dissolving the residue in a hot solution of ammonium nitrate which dissolves the uranium and leaves the vanadium undissolved; no phosphates should be present. It may also be removed by excess of sodium hydroxide or by neutralising the nitric acid solution with mercuric oxide and then adding mercurous nitrate.

L. DE K.

**Detection and Estimation of Traces of Antimony in presence of large quantities of Arsenic.** By GEORGES DENIGÈS (*Compt. rend.*, 1901, 133, 688—689).—If tin is used instead of zinc in contact with platinum for the detection of antimony by deposition on the platinum in the form of a dark stain, the reaction becomes much more delicate and will detect 0.002 mg. of antimony in 0.05 c.c. of hydrochloric acid (1 : 4) provided that the quantity of arsenic present does not exceed 5 mg. per c.c. The rapidity with which the stain appears is a function of the quantity of antimony present and for a given time the depth of the stain is also a function of that quantity. The reaction can be used quantitatively by making precisely similar tests with solutions containing known quantities of antimony.

A still more sensitive reaction is obtained with antimony caesium iodide. The antimony compound is dissolved in dilute hydrochloric acid (1 : 4) or dilute sulphuric acid (1 : 10), and the reagent is made by dissolving 1 gram of potassium iodide and 3 grams of caesium chloride in 10 c.c. of water. A drop of the antimony solution and one of the reagent are mixed and examined under the microscope, when the antimony caesium iodide is seen to form in yellow or garnet-red hexagonal lamellæ, often grouped in stellate macles. The reaction will detect 0.0001 mg. of antimony in presence of 500 times the quantity of arsenic. It is important that the quantity of arsenic does not exceed 50 mg. per c.c., as with a larger quantity iodine will probably be liberated. Quantitative results can be obtained by the method of comparison.

C. H. B.

**Analysis of White Metal Alloys.** By FRED IBBOTSON and HARRY BREARLEY (*Chem. News*, 1901, 84, 167—169).—Antimony as precipitated reduces solutions of stannic chloride in the cold very slowly, whereas pulverised smelted antimony is inactive. The authors therefore

employ the latter at the boiling point in place of iron for the estimation of tin. With finely powdered metal, the reduction takes place rapidly, and when complete the solution is allowed to cool in an atmosphere of carbon dioxide and titrated with iodine. One-fifth the volume of strong hydrochloric acid is usually employed, but in the presence of copper one-third the volume is used, and in the presence of lead there must be plenty of acid to prevent the formation of cuprous iodide in the one case, or lead iodide in the other. Iron, chromium, nickel, zinc, manganese, aluminium, bismuth, tungsten, phosphorus, sulphur, mercury, molybdenum, and cobalt are inactive or exert a negligible influence in the cold. Arsenic, however, is precipitated and carries some tin with it; and in the case of antimony, when iron is used for the reduction, the tin is all reduced before the appearance of the antimony, a result which serves as an indication that all the stannic chloride is reduced.

D. A. L.

**Estimation of Chloroform.** By WILLIAM A. PUCKNER (*Pharm. Arch.*, 1901, 4, 124—128).—The following process is recommended as being particularly suitable for the estimation of chloroform in a mixture of chloroform and ether. A quantity of the mixture equal to 0.05—0.2 gram of chloroform is put into a strong flask containing 10 c.c. of *N* alcoholic potassium hydroxide free from chlorine, the flask is closed with a sound cork, covered with cloth and tied down firmly. After gently mixing the liquids, the flask is put in boiling water for 3 hours. When cold, the contents are carefully neutralised with *N* sulphuric acid, using phenolphthalein as indicator, and the chlorine is then estimated by means of silver nitrate and potassium chromate. Or the cold liquid may be acidified with nitric acid and titrated by Volhard's thiocyanate process. From the amount of chlorine thus found, the percentage of chloroform in the mixture is readily calculated.

If the percentage of chloroform in the sample is quite unknown, it may be determined approximately by digesting 1 c.c. for an hour with 25 c.c. of *N* alcoholic potassium hydroxide and titrating the excess of alkali. One c.c. of *N* alkali consumed  $\times 0.02977$  equals the amount of chloroform per c.c.

L. DE K.

**Estimation of Cyanide in the presence of a Chloride.** By FRANK B. GATEHOUSE (*Chem. News*, 1901, 84, 197).—When silver nitrate is added to a solution of potassium cyanide, the soluble double cyanide,  $\text{KCN}, \text{AgCN}$ , is first formed, and no precipitate is obtained so long as there is cyanide in solution. Therefore, titration with *N*/10 silver nitrate until a permanent turbidity appears may be used to estimate the cyanide; each c.c. used = 0.013036 gram of potassium cyanide. An equal volume of the *N*/10 solution is then added, the burette read, potassium chromate introduced as indicator, and the chloride estimated in the usual way.

D. A. L.

**Estimation of Alcohol in Ether.** By FRANZ FREYER (*Chem. Centr.*, 1901, ii, 900; from *Zeit. landw. Versuchs-Wes. Oesterr.*, 4, 955—959).—The amount of alcohol and water is estimated by agitat-

ing 20 c.c. of the sample with a saturated solution of calcium chloride and noticing the diminution in volume. Twenty-five c.c. of the sample (which should not contain more than 1 gram of alcohol and water, otherwise it should be diluted with anhydrous ether) are put into an Erlenmeyer flask, mixed with 50 c.c. of a 10 per cent. solution of acetyl chloride in chloroform and the flask closed with an india-rubber cork, through which passes a separating funnel containing 100 c.c. of water. After the lapse of an hour, a little of the water is introduced, and the whole well shaken and then titrated with 2 *N* alkali, phenolphthalein being used as indicator. A blank experiment is then made with 50 c.c. of the acetyl chloride solution, mixed with anhydrous ether, which is titrated in the same manner. The difference in the two titrations represents the alcohol, inasmuch as by the action of alcohol on acetyl chloride only 1 mol. of free acid is formed, whilst water liberates 2 mols. One c.c. of 2 *N* alkali = 0.092 gram or 0.1157 c.c. of alcohol.

L. DE K.

**Quantitative Esterification and Estimation of Alcohols and Phenols.** By ALBERT VERLEY and FR. BÖLSING (*Ber.*, 1901, 34, 3354—3358).—Esterification takes place rapidly and completely when a mixture of acetic anhydride and pyridine is used in place of acetic anhydride. For quantitative esterification, a mixture of 120 grams of acetic anhydride and 880 grams of pyridine is used; this is titrated with standard alkali, and again after heating with a known weight of the alcohol or phenol. The method has been successfully used with ethyl alcohol, amyl alcohol, cinnamic alcohol, menthol, phenylglycol, glycerol, phenol,  $\beta$ -naphthol, guaiacol, saligenin, thymol, eugenol, carvacrol, and santalol, but geraniol, terpineol, vanillin, benzyl alcohol, and linalool could not be satisfactorily determined by this method.

T. M. L.

**Estimation of Eugenol in Oil of Cloves.** By ALBERT VERLEY and FR. BÖLSING (*Ber.*, 1901, 34, 3359—3362).—Eugenol can be satisfactorily estimated in oil of cloves by quantitative esterification with a mixture of acetic acid and pyridine, provided that other phenols and alcohols are absent. Umney's method (*Pharm. J.*, 1895, 25, [iii], 950), in which the oil is extracted with 10 per cent. alkali and the residue weighed, is liable to large errors; Thoms' method (*Abstr.*, 1892, 250) gives small values with oils rich in terpenes.

T. M. L.

**Nickel Salts as Reagents for Reducing Sugars.** By MAURICE DUYK (*Ann. Chim. anal. appl.*, 1901, 6, 364).—The reagent is best prepared by adding to 25 c.c. of a 20 per cent. solution of nickel sulphate 20 c.c. of aqueous sodium hydroxide of sp. gr. 1.33 and 3 grams of tartaric acid dissolved in 50 c.c. of water. A clear, slightly green liquid is thus obtained which does not change on boiling, but is at once reduced on adding a reducing sugar, with separation of a lower oxide having a brown, or even intense black, colour. The reagent is likely to be of great service in urine analysis, as it is not in the least affected by normal urine. Sollmann (*Abstr.*, 1901, ii, 535) has also applied nickel salts, but his conclusions differ somewhat from those of the author.

L. DE K.



**Detection of Sucrose in Plants by means of Invertin, and of Glucosides by means of Emulsin.** By EMILE BOURQUELOT (*Compt. rend.*, 1901, 133, 690—692).—The presence of sucrose in vegetable extracts is most conveniently detected, and its quantity estimated, by the action of invertase, the rotatory power of the liquid being determined before and after the action of the ferment. Invertase also hydrolyses gentianose and raffinose, but these substances are comparatively rare, and the products of hydrolysis are readily distinguished from those of sucrose. Emulsin may be employed with advantage in the same manner for the detection and estimation of glucosides. For example, the pericarp of *Cocos Yatai* and the seed of asparagus were found to contain a considerable proportion of sucrose but no glucosides, whilst the rhizome of *Scrophularia nodosa* contained a considerable quantity of a lævorotatory glucoside. C. H. B.

**Estimation of Starch in the Grain of Cereals.** By LÉON LINDET (*J. Pharm. Chim.*, 1901, [vi], 14, 397—400. Compare Abstr., 1897, ii, 525).—The process only differs from the one previously described in that, instead of collecting the starch on a tared filter, the amylaceous liquid is siphoned off, and the starch which is left behind is washed by decantation, and then hydrolysed with dilute sulphuric acid. The resulting glucose and dextrin are then estimated by means of Fehling's solution and the polarimeter. H. R. LE S.

**Estimation of Formaldehyde.** By LUDWIG VANINO and E. SEITTER (*Zeit. anal. Chem.*, 1901, 40, 587—589).—An excess of potassium permanganate strongly acidified with sulphuric acid oxidises formaldehyde quantitatively to carbon dioxide and water. The proportions recommended are 30 grams of concentrated sulphuric acid, 50 c.c. of water (mixed and cooled), 35 c.c. of *N*/5 permanganate, and 5 c.c. of a 1 per cent. solution of formalin. After 10 minutes, the excess of permanganate is titrated by an empirical solution of hydrogen peroxide. The results agree well with those obtained by Romijn's method, which is adopted by the Verein für Chemische Industrie in Mainz (Abstr., 1900, ii, 326). M. J. S.

**Some sources of Error in the Estimation of the Volatile Acidity of Wines.** By CURTEL (*Ann. Chim. anal. appl.*, 1901, 6, 361—364).—The author states that the total acidity of a wine as found by direct experiment is always less than the sum of acids existing in it, and has investigated the cause of this phenomenon.

The volatile acids will be found too high if the wine should contain neutral acetates or similar salts, as, on boiling, part of the acid is liberated by the action of potassium hydrogen tartrate, or even tannic acid. Several experiments are given showing that the volatile acids thus formed may be equivalent to as much as 0.06 per cent. of acetic acid. Another serious source of error is the introduction of carbon dioxide by means of the steam which is passed through the wine when estimating the volatile acids. The steam should be generated from recently boiled distilled water. The error may amount to 0.029 per cent. expressed as acetic acid. A third, although less important, source

of error is the presence of ethyl acetate, which, when boiled with water, yields a faintly acid distillate, which may account for 0.009 per cent. of volatile acid.

In order to avoid these errors, the author first estimates the total acidity, less carbon dioxide. Twenty-five c.c. of the wine and 25 c.c. of water are introduced into a small flask furnished with a doubly perforated cork and placed on a heated sand-bath, and steam is passed through at such a rate that the liquid does not undergo any sensible alteration in volume. After the lapse of an hour, the acidity is again determined, the difference between the two experiments being the volatile acidity.

L. DE K.

**Supposed Use of Oxalic Acid for the Preparation of Hydrogen Peroxide.** By AUGUSTE NICOLLE (*Chem. Centr.*, 1901, ii, 834—835; from *Mon. scient.*, [iv], 15, ii, 576. Compare Abstr., 1901, ii, 622).—The following process is proposed for the detection of oxalic acid in commercial hydrogen peroxide. Five hundred c.c. of the sample are evaporated to dryness on the water-bath with addition of pure sodium hydroxide, the well-dried residue is dissolved in dilute nitric acid, about 50 c.c. of water are added, together with calcium nitrate or chloride, and then excess of ammonia. The liquid is heated, the precipitate washed free from soluble salts by decantation, and then heated at 50° with 30 c.c. of sulphuric acid of sp. gr. 1.2—1.4. The filtrate and washings are evaporated on the water-bath in a vacuum until about 30 c.c. are left; on cooling, any oxalic acid will crystallise, and may then be further identified. The author has not as yet succeeded in detecting oxalic acid in commercial hydrogen peroxide.

L. DE K.

**Probable Errors of Analysis resulting from the Presence of Salicylic Acid in Strawberries.** By L. PORTES and A. DESMOULIÈRES (*J. Pharm.*, 1901, [vi], 14, 342—351).—Compare this vol., ii, 40.

**New Process for the Detection and Estimation of Salicylic Acid.** By HENRI PELLET (*Ann. Chim. anal. appl.*, 1901, 6, 364—365).—Twenty c.c. of the liquid to be tested are acidified and boiled down in a beaker and from time to time a cold stirrer is held over the liquid so as to condense the vapour, which is then tested for salicylic acid by dropping it on a slightly greased porcelain slab on which are placed minute drops of ferric chloride. The author has noticed that no reaction will be obtained until the salicylic acid reaches the concentration of 0.06—0.07 gram per litre. Supposing, therefore, that the liquid has to be boiled down to 6 c.c. before the test is obtained, then the 20 c.c. contain  $10:6 = 0.0006—7$  or about 0.0004 gram of salicylic acid. Liquids containing much salicylic acid must first be suitably diluted.

When dealing with wines, the process should be applied to the product resulting from the extraction of the wine with benzene.

L. DE K

## General and Physical Chemistry.

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**A Method for the production of Coloured Flames.** By STSCHEGLAYEW (*Zeit. physikal. Chem.*, 1901, 39, 111—113).—To obtain a flame coloured by a metallic salt, lasting for a considerable time in a steady state, the author suggests a blast of air blown horizontally into the surface layer of a saturated solution of the salt and then forming the air current of a bunsen burner. It is stated that if a motor be employed to yield a regular air stream at about 60 mm. pressure, most satisfactory results are obtained.

L. M. J.

**Photographs of Spark Spectra. I. Ultra-violet Spark Spectra of Iron, Cobalt, Nickel, Ruthenium, Rhodium, Palladium, Osmium, Iridium, Platinum, Potassium Chromate, Potassium Permanganate, and Gold.** By WALTER E. ADENEY (*Trans. Roy. Dublin Soc.*, 1901, ii, 7, 331—338).—Reference must be made to the photographic reproductions accompanying the paper. In these, many lines observed by Eder and Valenta, as well as by Exner and Haschek, are absent, probably owing, in the majority of cases, to the different methods of sparking employed.

J. C. P.

**Theory of Fluorescence.** By WOLDEMAR VOIGT (*Arch. Néer. sci. exact. nat.*, 1901, [ii], 6, 352—366).—Fluorescent and phosphorescent phenomena are due to free, incoherent vibrations within the excited substance. The author discusses the electron theory and from results so far obtained concludes that the molecules of fluorescing substances are capable of existing in two conditions, in which the electrons have different periods of vibration. The change from one state to the other is conditioned by molecular relationships, but an exciting light wave has also the power of aiding or starting the transition. The electrons pass into the new condition with speeds and elongations which are influenced by the motion given to them by the exciting wave in the old condition and they perform free, incoherent vibrations with a period corresponding with the new condition. The periods of vibration in the two conditions are very different and one is damped to a much greater extent than the other.

J. McC.

**Chemical Effects produced by Radium Radiations.** By HENRI BECQUEREL (*Compt. rend.*, 1901, 133, 709—712).—Various chemical effects produced by radiations from radium have been already observed, as, for example, the action on silver gelatino-bromide, or barium platinocyanide, destructive action on the skin, the coloration produced in rock salt, sylvite, and in varieties of glass or porcelain. The author has observed the following additional actions. (1) The transformation of yellow phosphorus into red, which may be brought about by immersing a sealed glass tube containing radium, enveloped in aluminium foil, into a glass vessel containing the phosphorus, the whole being kept in the dark. The transformation does not continue

after the removal of the radium. (2) The reduction of mercuric chloride by oxalic acid which takes place in the dark if the radium tube be placed in the mixed solutions. (3) Destruction of the germinative power of seeds by exposure to the radiation before planting. Mustard and cress seeds were divided into two portions, of which one was exposed for a week or more to the radiations; none of the seeds so exposed germinated, whilst of the others used for comparison, 80 per cent. germinated.

L. M. J.

**Induced Radioactivity excited by Radium Salts.** By P. CURIE and A. DEBIERNE (*Compt. rend.*, 1901, 133, 931—934. Compare Abstr., 1901, ii, 216, 298).—The phenomena of induced radioactivity excited by radium salts are more regular, and the activity is more intense, when an aqueous solution is used instead of the solid salt. The intensity of the induced activity is the same for all substances, whatever their chemical nature, under the same conditions, and is independent of the pressure of the gas surrounding the exciting and excited bodies. The induced radiation, like the exciting radiation, consists of some rays which are deflected in a magnetic field and some which are not. Other conditions being the same, the intensity of the induced radiation depends on the free space in front of the excited body; if, for example, several copper plates are placed parallel with one another and about 1 mm. apart, they acquire little activity, but if about 30 mm. apart they all become strongly active. The intensity of the radioactivity which can be excited in a given enclosure depends only on the quantity of radium introduced into it in the form of a solution. The glass of the enclosing vessel generally becomes luminous, and the luminosity finally acquired by any part of the vessel is independent of the position of the radium solution. If a radium solution and zinc sulphide are placed in separate flasks connected by a glass tube bent twice at right angles, the sulphide becomes and remains phosphorescent, and at the same time exhibits radioactivity, the intensity of the activity being independent of the phosphorescence and equal to that which would be acquired by any other substance under the same conditions.

C. H. B.

**Influence of Radioactive Substances on the Luminescence of Gases.** By ALEXANDER DE HEMPTINNE (*Compt. rend.*, 1901, 133, 934—935).—Gases subjected to the influence of radioactive substances become luminous under the electric discharge at higher pressures than under normal conditions. In this respect, the Becquerel rays, therefore, resemble Röntgen rays; in both cases also the phenomenon is more marked the higher the molecular weight of the gas.

C. H. B.

**Electromotive Efficiency of the Elementary Gases. II.** Note by EMIL BOSE (*Zeit. physikal. Chem.*, 1901, 39, 114).—A note in which the author acknowledges priority of Richarz regarding some points of his work on this subject (Abstr., 1901, ii, 589).

L. M. J.

**Observations on the Determination of Transport Numbers of the Ions during Electrolysis of their Solutions. The Behaviour of Diaphragms during the Electrolysis.** By WILHELM HITTORF (*Arch. Néer. sci. exact. nat.*, 1901, [ii], 6, 671—688).—The

transport numbers recently determined do not in all cases agree with the early determinations of the author, and the divergence is greater than can be accounted for by experimental error. This led the author to an examination of the influence of diaphragms of porous porcelain, fine silk, and animal membrane in the conductivity cell. These diaphragms are used to keep the concentration of the electrolyte in the middle unchanged by preventing diffusion. In the case of copper sulphate, silver nitrate, and the chlorides of potassium, ammonium, sodium, barium, calcium, magnesium, and cadmium, the transport number is the same whether no diaphragm or one of silk or porous porcelain be used. With cadmium chloride, when animal membrane is used, the transport number of the cation is smaller than when no diaphragm is used. The animal membrane has the power of separating the solution into a more and a less concentrated part, and the less concentrated solution goes in the direction of the negative current, in this way leaving the solution round the cathode more dilute than it would be if no diaphragm were used. The use of animal membrane as diaphragm is without influence on the transport numbers of the ions of the chlorides of potassium, ammonium, and sodium. J. McC.

**Dissociation of certain Acids, Bases, and Salts at Different Temperatures.** By HARRY C. JONES and JAMES M. DOUGLAS (*Amer. Chem. J.*, 1901, **26**, 428—453).—The substances investigated were hydrochloric, nitric, and sulphuric acids, potassium hydroxide, chloride, bromide, iodide, nitrate, sulphate and permanganate, sodium nitrate and ammonium nitrate. The temperature coefficient of conductivity increases (1) with dilution for acids, bases, and salts; (2) with rise of temperature for salts; in the case of acids and bases, change of temperature has no appreciable effect on the temperature coefficient of conductivity. The amount of dissociation in solutions of the above substances, as measured by the conductivity, is independent of the temperature. This fact, in conjunction with the observation that the conductivity of the solutions increases with the temperature, shows that rise of temperature affects the velocities of the ions. J. C. P.

**Effect of Temperature and Moisture on the Emanation of Phosphorus, and a Distinction in the Behaviour of Nuclei and of Ions.** By CARL BARUS (*Amer. J. Sci.*, 1901, [iv], **12**, 327—346).—A physical paper dealing with the ionisation of air by its passage over phosphorus at various temperatures. J. C. P.

**Pressure as Supplement to Temperature in the Phenomenon of Inflammation.** By WALTHER SPRING (*Arch. Néer. sci. exact. nat.*, 1901, [ii], **6**, 257—261).—No combination took place on subjecting an intimate mixture of 2 mols. of cupric oxide and 3 mols. of sulphur to a pressure of 10,000 atmospheres. Combination took place violently when the pressure on a mixture of 2 mols. of cuprous oxide and 3 mols. of sulphur rose to 8000 atmospheres; the pressure was increased gradually so that no heating by compression took place. Sulphur dioxide was formed and the residue consisted only of cuprous sulphide ( $2\text{Cu}_2\text{O} + 3\text{S} = 2\text{Cu}_2\text{S} + \text{SO}_2$ ). The ignition temperature of this

mixture at the ordinary pressure is about  $126^{\circ}$ , and pressure to the extent of 8000 atmospheres has the effect of lowering this by more than  $100^{\circ}$ . The ignition temperature of the mixture of cupric oxide and sulphur could not be determined for the sulphur inflamed at  $250^{\circ}$ , but it must be higher than this. It would appear that the point of inflammation is a function of the pressure, and the experiments are being continued to ascertain if this is quite general. J. McC.

**Isotherms for Mixtures of Hydrogen Chloride and Ethane.** By N. QUINT GZM (*Zeit. physikal. Chem.*, 1901, 39, 14—26).—Isotherms for hydrogen chloride, ethane, and mixtures containing 86.82, 59.68, 38.33, and 28.59 per cent. of hydrogen chloride respectively, were determined at temperatures from  $15^{\circ}$  to  $55^{\circ}$  and the critical phenomena investigated. The mixtures behave very similarly to the mixture of nitrous oxide and ethane investigated by Kuenen (Abstr., 1896, ii, 10), and the author uses his results to test the validity of van der Waals' expression in the case of mixtures. Satisfactory agreement between calculated and observed numbers is obtained.

L. M. J.

**Minimum Value of the Total Heat of Combination.** By ROBERT DE FORCRAND (*Compt. rend.*, 1901, 133, 681—684).—The author has previously enunciated the relation  $(L+S)/T=30$ , or, in the case of a dissociative change in which a gas is produced,  $(L+S+q)/T=30$ , where  $q$  is the heat of combination. In the case of a gas and a dissociable compound of this gas, therefore,  $(L+S)/T = (L+S+q)/T' = 30$ , hence  $q/(T'-T)=30$ , that is, the heat of combination is proportional to the elevation of the boiling point, and when  $T'-T$  is small,  $L+S+q$  (or the total heat of combination,  $Q$ ) approximates to  $L+S$ . This deduction is tested chiefly by examples of compounds of ammonia, with metallic salts, in which the value  $T'$  is but slightly greater than  $234.5^{\circ}$ , the boiling point of ammonia, for each of which also the total heat of combination is about 7 to 8 Cal., the value  $L+S$  for ammonia being calculated as 7.03 Cal. (Abstr., 1901, ii, 372, 594). L. M. J.

**Determination of the Heat of Dissociation and of Combustion of Acetylene, Ethylene, and Methane.** By WILLIAM G. MIXTER (*Amer. J. Sci.*, 1901, [iv], 12, 347—357).—The heat of dissociation of acetylene is found by explosion in a bomb to be 53300 cal. (Thomsen, 47770 cal.; Berthelot, 51400 cal.); the heat of combustion of acetylene is 313800 cal. (Thomsen, 310050 cal.; Berthelot, 315700 cal.). The heat of dissociation of ethylene was found by exploding a mixture of ethylene and acetylene, and subtracting the thermal effect due to the acetylene; the author's results vary a good deal, but indicate that ethylene may be more endothermic than has been supposed. The heat of combustion of ethylene is 345800 cal. (Thomsen, 333350 cal.; Berthelot, 341100 cal.). The heat of dissociation of methane, determined in the manner described for ethylene, is found to be -19000 cal. (Thomsen, -21170 cal.; Berthelot, -21500 cal.).

J. C. P.

**New Method of representing Heats of Solution.** By HENDRIK W. BAKHUIS ROOZEBOOM (*Arch. Néer. sci. exact. nat.*, 1901, [ii], 6, 430—441).—The heat of solution can best be represented diagrammatically by referring the concentration of the solution, not as is usually done, to the number of mols. of solvent per mol. of dissolved substance, but so that the sum of the number of molecules of solvent and dissolved substance is equal to unity (or 100). The advantage gained is that the curve obtained is a complete one and does not run to infinity. Three forms of curve for heat of mixture of liquid components are known : (1) positive heats only ; (2) negative heats only ; (3) positive and negative heats according to the relative quantities of the components. The heat of solution of solid substances can be easily obtained from these heat of mixture curves if the heat of fusion is known, and from them also can be deduced the theoretical heat of solution, that is, the heat change which occurs when 1 mol. of salt is dissolved in an infinite quantity of its saturated solution. J. McC.

**Fusion and Crystallisation. The Theory of Tammann.** By PIERRE DUHEM (*Arch. Néer. sci. exact. nat.*, 1901, [ii], 6, 93—102).—According to the Clausius formula  $dT/dP = 1/E \cdot T/L \cdot (v' - v)$  for the variation of the point of fusion with the pressure, in which  $P$  is the pressure,  $T$  the fusion point at pressure  $P$ ,  $L$  the heat of fusion at pressure  $P$  and temperature  $T$ ,  $v$  the specific volume of the crystalline phase at  $P$  and  $T$ ,  $v'$  the specific volume of the isotropic phase at  $P$  and  $T$ , and  $E$  the mechanical equivalent of heat, since the values of  $1/E$  and  $T/L$  are positive, the sign of  $dT/dP$  must be the same as that of  $(v' - v)$ . It is probable that for some substances the value of  $(v' - v)$  is positive up to a maximum value of  $P$ , then assumes the value 0, and finally becomes negative ; in these cases, the curve of fusion is concave towards the pressure axis on a system of coordinates.

Tammann has found that when an isotropic phase is gradually cooled, the tendency to crystallise is small just below the fusion point ; it increases to a maximum as the temperature falls and at low temperatures again becomes small. Tammann interprets this by assuming that if the temperature be lowered sufficiently and the pressure kept constant, a second fusion point is reached, that is, a second temperature at which the isotropic and the crystalline phases are in equilibrium. The author shows that the phenomena can be better explained by assuming, instead of a curve of second fusion, a *line of false equilibrium*. Tammann's view assumes that there will always be a line along which  $(v' - v) = 0$ , and a line along which  $L = 0$ . The new view does not necessitate these lines, which, indeed, are in some cases difficult to admit. J. McC.

**Folding Point Curves in Ternary Systems.** By FRANZ A. H. SCHREINEMAKERS (*Arch. Néer. sci. exact. nat.*, 1901, [ii], 6, 170—192. Compare Abstr., 1901, ii, 224, 305, 372, 436, 641).—The author continues the discussion of the vapour pressure of ternary mixtures. A folding point indicates a critical solution, as in this point two liquid layers must be identical. The conditions for critical liquids of the first and second order are developed, and it is shown that if on the curve of

a critical liquid of the first order under constant pressure there rests a critical liquid of the second order, then at the point of contact the temperature must be either a maximum or a minimum. The author develops a formula by means of which it can be foretold whether the temperature at which two liquid layers are identical is raised or lowered by addition of a third component. A critical liquid at a given temperature can only be in equilibrium with vapour at a certain definite pressure, and change of temperature alters, not only the pressure, but also the composition of both liquid and vapour. The effect of change of pressure is also fully discussed. J. McC.

**An Equation for Osmotic Pressure in Concentrated Solution.** By C. H. WIND (*Arch. Néer. sci. exact. nat.*, 1901, [ii], 6, 714—726).—From considerations similar to those employed by van der Waals in the development of the gas equation of condition, the author deduces the equation of condition in concentrated solution,  $RT = [N + (a - a')/V^2] [V - \theta b^2/V]$ , as a more complete statement of van't Hoff's law.  $N$  is the osmotic pressure,  $V$  the total volume of the system, and  $a$ ,  $a'$ ,  $b$  and  $\theta$  are constants. This equation differs from that of van der Waals inasmuch as the pressure correction may be negative (if  $a'$  is greater than  $a$ ) and in that the volume correction contains  $V$  in the denominator. The equation correctly expresses the results obtained by Ewan (*Abstr.*, 1900, ii, 195) and by Byl (*Proefschrift, Amsterdam*, 1901). J. McC.

**Neutral Salts.** By KURT ARNDT (*Zeit. anorg. Chem.*, 1901, 28, 364—370).—The degree of dissociation of 0.1*N* solutions of the following are: HCl, 0.91; HNO<sub>3</sub>, 0.92;  $\frac{1}{2}$ H<sub>2</sub>SO<sub>4</sub>, 0.58; KOH, 0.89; NaOH, 0.84. In solutions of chloride and nitrate of potassium and sodium, there will be about the same quantity of hydrogen and hydroxyl ions produced by hydrolysis. Since sulphuric acid is less dissociated than potassium or sodium hydroxides, in the solution of the sulphates there will be a slight excess of hydroxyl ions. This excess is too small to be detected by indicators, but the influence of potassium sulphate on the catalysis of ethyl acetate is very different from that of chlorides or nitrates and resembles that of alkalis (Arrhenius, *Abstr.*, 1888, i, 340). The inversion of sucrose by hydrochloric acid is increased by addition of chlorides; the inversion by sulphuric acid is diminished by potassium or sodium sulphate (Spohr, *Abstr.*, 1885, 1181). The small quantity of the hydroxyl ion can be even more sharply detected by its influence on the birotation of dextrose. The influence of sulphates on the rotation of dextrose is similar to that of weak bases (Levy, *Abstr.*, 1895, i, 586; Trey, *Abstr.*, 1897, ii, 299). J. McC.

**Velocity of Solution of Solid Substances. II.** By LUDWIK BRUNER and STANISLAW TOLLOCZKO (*Zeit. anorg. Chem.*, 1901, 28, 314—330. Compare *Abstr.*, 1901, ii, 10).—Experiments on the velocity of solution of benzoic acid cast into a cake and rotated in water show that some of the solid is mechanically rubbed off and becomes suspended in the solution. Drucker's results (*Abstr.*, 1901, ii, 376) are vitiated by this circumstance. From experiments with



alabaster, it is proved that the rate of rotation of the plate has a great influence on the velocity of solution, but the volume of the liquid used is without influence. Hydrogen ions are without influence on the speed of solution of calcium sulphate. The velocity of solution is dependent on the structure of the solid substance, smooth gypsum crystals being dissolved more slowly than the granular alabaster.

J. McC.

**The Investigation of Complex Compounds.** By GUIDO BODLÄNDER (*Chem. Centr.*, 1901, ii, 1109—1111; from *Sonderabdruck aus der Festschr. zur Feier des-siebzigsten Geburtstages Richard Dedekind*, 153—182).—Complex compounds are often formed in solution by the combination of a sparingly soluble compound with a molecule or an ion of a soluble one. In some cases, as, for instance, when silver cyanide dissolves in solutions containing cyanogen ions, the quantity of the more insoluble compound which goes into solution is equivalent to that of the soluble compound, whilst in others, the proportions vary with the quantities present. The solution of silver chloride by ammonia or of cuprous chloride by hydrochloric acid is an example of the latter type. In such cases, the law of mass action may be applied, and an indication of the composition of the dissolved ions may be derived from the solubility of the less soluble in an excess of the soluble component. Assuming, for instance, the formula  $\text{Cu}_m\text{Cl}_{m+n}$  to represent the complex ions in a solution of cuprous chloride in presence of a soluble chloride, then  $(\text{CuCl})^m\text{Cl}^n = \text{Cu}_m\text{Cl}_{m+n}k$ , and since the quantity of active cuprous chloride is constant,  $\text{Cl}^n = \text{Cu}_m\text{Cl}_{m+n}k_2$ . This gives no indication, however, of the value of  $m$ , for if  $n=2$  then the formula of the complex ions may be  $\text{CuCl}_3$ ,  $\text{Cu}_2\text{Cl}_4$ , or  $\text{Cu}_3\text{Cl}_5$ , &c. The formula of the complex ions may be calculated from measurements of the *E.M.F.* between electrodes of the same metal as that in the complex in a concentration cell containing two solutions which must have either the same concentration in respect of the complex and different concentrations of the soluble component or *vice versa*. The *E.M.F.* between silver electrodes immersed in solutions containing equal quantities of silver but unequal quantities of ammonia may be calculated from the law of mass action. Assuming the formula of the complex ions to be  $\text{Ag}_m(\text{NH}_3)_n$ , then  $k[\text{Ag}_m(\text{NH}_3)_n] = \text{Ag}^m \cdot (\text{NH}_3)^n$  for one solution and  $k[\text{Ag}_m(\text{NH}_3)_n]_1 = \text{Ag}_1^m (\text{NH}_3)_1^n$  for the other. Since the concentration of the complex ions is the same in both solutions,  $(\text{Ag}:\text{Ag}_1)^m = [(\text{NH}_3)_1:(\text{NH}_3)]^n$ .

Neglecting the difference of potential at the boundary of the two solutions, then the *E.M.F.* is

$$E = 0.058 \log(\text{Ag}:\text{Ag}_1) = 0.058_{n/m} \log[(\text{NH}_3)_1:(\text{NH}_3)].$$

If the concentration of the free ammonia is the same in both solutions but that of the complex ions different, then :

$$[\text{Ag}_m(\text{NH}_3)_n]_1 : [\text{Ag}_m(\text{NH}_3)_n] = (\text{Ag}_1:\text{Ag})^m, \text{ and}$$

$$E_1 = 0.058 \log(\text{Ag}_1:\text{Ag}) = 0.058_{m/n} \log([\text{Ag}_m(\text{NH}_3)_n] : [\text{Ag}_m(\text{NH}_3)_n]_1).$$

Hence, from  $E$  and  $E_1$ ,  $m$  and  $n$  can be calculated.

It has been found by this method that silver chloride or silver nitrate in ammoniacal solution contains the ion  $\text{Ag}(\text{NH}_3)_2$ , cuprous oxide in ammoniacal solution the ion  $\text{Cu}(\text{NH}_3)_2$ , and cuprous chloride

in solutions of chlorides the ion  $\text{CuCl}_2$  or  $\text{CuCl}_3$ , according to the concentration.

E. W. W.

**Dissolution of Metals.** By T. ERICSON-AURÉN and WILHELM PALMAER (*Zeit. physikal. Chem.*, 1901, **39**, 1—13).—The law of mass action cannot be applied to calculate the velocity of dissolution of zinc in acids, as the values so calculated do not agree with the experimental results. The authors consider that dissolution is purely electrolytic and occurs solely as a result of local currents; to this is due the slow velocity of dissolution of pure metals. On this assumption, an expression is deduced for the rate of dissolution of a metal in acids of any concentration, the expression, however, involving an unknown quantity, the resistance capacity. This may, however, be deduced from one set of determinations and the velocity of dissolution under other conditions then calculated. The values so obtained were found to agree well with those determined experimentally. The temperature coefficient between  $10^\circ$  and  $50^\circ$  was found to be in general about 1.5 to 2 per cent. per degree. This is far smaller than the usual temperature coefficient of a chemical reaction, but is approximately that of the increase of *E.M.F.*, a result in accord with the theoretical views.

L. M. J.

**Velocity of Decomposition of Ammonium Nitrite.** By KURT ARNDT (*Zeit. physikal. Chem.*, 1901, **39**, 64—90).—The velocity of decomposition of aqueous solutions of ammonium nitrite was determined at temperatures varying from  $60^\circ$  to  $80^\circ$ , and at concentrations varying from 0.6 'molar' to 0.3 'molar.'\* It was found that in the solutions of the higher concentration the increase of temperature from  $60^\circ$  to  $80^\circ$  caused an increase in the rate of evolution of nitrogen from 0.37 c.c. per min. to 3.2 c.c. per min. It was observed that the addition of small quantities of acid increases to a very great extent the velocity of decomposition, whilst ammonia causes an equally marked decrease. This suggested that the decomposition is really due to interaction between the ammonium nitrite and nitrous acid produced by hydrolytic dissociation. From the effect of the addition of sulphuric acid, it was calculated, on this assumption, that the hydrolytic dissociation is about 0.25 per cent. at  $70^\circ$ , a value which agreed with that calculated from the effect of the addition of ammonia. Ammonium sulphate increases the velocity, probably owing to the increase of undissociated ammonium nitrite, whilst sodium nitrite, by increasing also the free nitrous acid, causes a more marked increase of the velocity. The addition of other neutral salts causes, as expected, a decrease of the decomposition. That the decomposition is not a simple change is also indicated by the approximate proportionality of the velocity to the third power of the concentration.

L. M. J.

**Equilibrium between Carbonates and Bicarbonates in Aqueous Solution.** By FRANK K. CAMERON and LYMAN J. BRIGGS (*J. Physical Chem.*, 1901, **5**, 537—555).—Solutions of sodium carbonate or

\* The term 'molar' is used by the author to indicate the molecular weight of a substance in grams per litre.

of hydrogen sodium carbonate attain a state of equilibrium in which both salts are present, the composition being dependent on the total concentration, the temperature, and the pressure of carbon dioxide in the vapour phase. The concentration of the two salts in solution was determined by titration with hydrogen potassium sulphate with (1) phenolphthalein, (2) methyl-orange as indicator. Curves are given which show the percentage present as normal carbonate at different concentrations and temperatures. At all temperatures, the quantity of normal salt rapidly increases with the concentration until a concentration of about  $0.4N$ , when it remains almost constant; the proportion of normal carbonate also increases with rise of temperature. In certain solutions, the author considers a maximum in the curve is indicated, but fuller examination is deferred. Solutions of potassium carbonate gave perfectly analogous results. Calcium carbonate exists in solution almost entirely as the hydrogen salt, but solutions of magnesium carbonate may contain 50 per cent. of the normal salt. In both cases, the equilibrium and total solubility are greatly affected by the pressure of the carbon dioxide.

L. M. J.

**Precipitation of Colloids by Electrolytes.** By WILLIS R. WHITNEY and J. E. OBER (*J. Amer. Chem. Soc.*, 1901, 23, 842—863).—When 30 c.c. of a 1 per cent. solution of barium chloride were added to 200 c.c. of a 1 per cent. colloidal arsenious sulphide solution, complete precipitation of the arsenious sulphide immediately occurred; it was found that the precipitate contained 0.0152 gram of barium and that an equivalent amount of hydrogen chloride had been produced. By employing an arsenious sulphide solution of half the above strength, it was shown that the composition of the precipitated colloid is independent both of the concentration of its solution and of that of the barium salt. Experiments in which the chlorides of calcium, strontium, and potassium were used showed that the precipitated colloid contained the metals, barium, strontium, calcium, or potassium in the proportions of their equivalent weights; this result supports Whetham's hypothesis (*Abstr.*, 1900, ii, 62).

An index to the literature of colloids is appended.

E. G.

**The Standard for Atomic Weights.** By THEODOR W. RICHARDS (*Zeit. anorg. Chem.*, 1901, 28, 355—360. Compare *Abstr.*, 1901, ii, 231, 379).—The author supports the proposal of the International Commission to take as standard  $O=16$ . On pedagogic grounds, objection cannot be taken to this if, in the development of Avogadro's rule, use is made of the densities (experimental) of the gases, that is, the actual weights of 1 litre of the various gases at  $0^\circ$ , instead of "specific gravities."

J. McC.

**Mathematical Expression of the Periodic Law.** By S. H. HARRIS (*J. Physical Chem.*, 1901, 5, 577—586).—The author shows sundry connections between the atomic weights of elements in different series and calculates the atomic weights of a number of unknown elements to fill the blank spaces in the periodic table.

L. M. J.

**Purification of Gases.** By L. E. O. DE VISSER (*Rec. Trav. Chim.*, 1901, [ii], 20, 388—393).—Stas has frequently emphasised the

incomplete purification of gases effected by passing them through tubes containing absorbent solids or liquids; a complete purification can, however, easily be obtained by passing the gas first through a layer of cotton wool which has previously been impregnated with a solution of the absorbent solid and dried in the air and subsequently through closely packed, pure cotton. If the gas attacks the latter, asbestos or fine-threaded glass wool may be used. In this way, carbon dioxide, generated from marble and hydrochloric acid, can be entirely freed from hydrogen chloride, although Stas has shown the latter to be present in the gas purified by passage through aqueous and solid sodium hydrogen carbonate.

W. A. D.

**A New Method of Manipulating Liquefied Gases in Sealed Tubes.** By HENRI MOISSAN (*Compt. rend.*, 1901, 133, 768—771).—When a current of air at  $18^{\circ}$  is passed through a mixture of solid carbon dioxide and ethyl or methyl alcohol, the temperature obtained is constantly  $-85^{\circ}$ ; with methyl chloride or aldehyde,  $-90^{\circ}$ ; with ethyl acetate,  $-95^{\circ}$ , and with acetone,  $-98^{\circ}$ . If the current of air is previously cooled to  $-80^{\circ}$ , the temperature obtained with the solid dioxide and acetone is  $-110^{\circ}$ . For lower temperatures, recourse must be had to liquid air or liquid oxygen.

When liquefied gases have to be sealed up in glass tubes, the operation is greatly simplified by first cooling the tube, so that the gas becomes solid. For a pressure of 200 atmos., the tube should be of 10 mm. external and 6 mm. internal diameter; for higher pressures, 7 mm. external and 3 mm. internal diameter; and for pressures as high as 300 atmos., 6 mm. external and 1.5 mm. internal diameter. The method is applicable when the liquefied gas is to act on some other substance, and if, after the reaction is finished, the tube is again strongly cooled before being opened, the products of the reaction can be distilled off fractionally. The method is not, however, applicable to reactions in which hydrogen is liberated. The author calls attention to the importance of allowing glass tubes which have been strongly cooled to return very slowly to the ordinary temperature.

C. H. B.

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### Inorganic Chemistry.

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Place of Hydrogen in the Periodic System. By BOHUSLAV BRAUNER (*Chem. News*, 1901, 84, 233—234).—A theoretical paper dealing mainly with the question as to whether hydrogen should be regarded as the first member of the halogen group, or whether the old view that it should stand at the head of the first group is still most in accordance with facts. D. A. L.

Positive and Negative Halogen Ions. By JULIUS STIEGLITZ (*J. Amer. Chem. Soc.*, 1901, 23, 797—799).—Attention is drawn to

the existence of positive chlorine ions in aqueous solutions of chlorine and hypochlorous acid, experimental proof of which is furnished by the work of Jakowkin (Abstr., 1899, ii, 736). E. G.

**Formation of Ozone.** By ALBERT LADENBURG (*Ber.*, 1901, **34**, 3849—3851).—In preparing ozone by means of the 'silent discharge,' the proportion of ozone reaches a maximum for intermediate values of the current strength, but increases progressively with falling temperature. The maximum percentage recorded is 10.79. T. M. L.

**Production of Ozone.** By A. CHASSY (*Compt. rend.*, 1901, **133**, 789—791).—The quantity of ozone formed in a Berthelot's apparatus at 20° increases with the time, according to a law which is independent of the intensity of the discharge. The curve representing the rate of increase is asymptotic to a line parallel with the axis of time, and the quantity of ozone formed tends towards a limit which depends on the temperature and is independent of the intensity of the discharge. The formation of a given quantity of ozone requires less expenditure of energy in the form of electric discharge when the percentage of ozone is low than when it is high. C. H. B.

**Decomposition of Potassium Iodide Solutions by Ozone.** By KARL GARZAROLLI-THURNLACKH (*Monatsh.*, 1901, **22**, 955—975. Compare Brunck, Abstr., 1900, ii, 572; Péchard, Abstr., 1900, ii, 536).—In the product obtained by the action of ozone on solutions of potassium iodide, the amount of iodine which could be extracted by carbon disulphide was determined by titration with potassium arsenite; the iodine present as hypoiodite or other compound and the total iodine were also estimated. When a concentrated solution of potassium iodide has been exposed to the action of ozone for five minutes, the solution contains iodine, hypoiodite, iodate, periodate, and potassium hydroxide. Further changes then take place, the quantity of hypoiodite and periodate gradually decreases, the former ultimately disappearing, whilst the amounts of iodine, potassium hydroxide, and iodate increase. Conditions more favourable for the formation of periodate, but less favourable for that of hypoiodite, are obtained by passing the ozone into the solution of the iodide. Attempts to obtain direct evidence of the presence of potassium peroxide or hydrogen peroxide failed, however. The fume which is formed when ozone acts on potassium iodide contains an iodine oxide which is attacked by potassium arsenite.

By the action of ozone on a solution of potassium bromide, hypobromite and bromate are formed together with some bromine.

E. W. W.

**Pure Tellurium and its Atomic Weight.** By PAUL KÖTHNER (*Annalen*, 1901, **319**, 1—58).—The communication contains a bibliography of the subject and a discussion of the relationship of tellurium to its neighbouring elements in the periodic classification. Tellurium may be separated from its common impurities (copper, silver, gold,

bismuth, antimony, arsenic, and selenium) by dissolving the crude substance in hydrochloric acid containing a little nitric acid, evaporating off the excess of the latter reagent, diluting the cooled solution with water until the deep yellow colour of tellurium tetrachloride disappears, filtering from the precipitate of silver chloride and the oxychlorides of antimony and bismuth, and treating the warm filtrate with sulphur dioxide. The precipitated metalloid is again subjected to the foregoing treatment and fractionally precipitated by the reducing agent. Three fractions are employed, and after repeating the operation two or three times the middle fraction consists of pure tellurium; the first portions contain arsenic, whilst the third fraction shows traces of copper and gold. The element may be obtained in a crystalline form by passing sulphur dioxide into a hot solution of the tetrachloride in concentrated hydrochloric acid (20.3 per cent.); the crystals being opaque with a silvery lustre.

Telluric acid, prepared by Staudenmaier's method (Abstr., 1896, ii, 96), even after repeated crystallisation, exhibits, in its spectrum, lines characteristic of silver, copper, and antimony.

The basic nitrate,  $\text{OH} \cdot \text{TeO} \cdot \text{O} \cdot \text{TeO} \cdot \text{ONO}_2$ , employed by Norris, Fay, and Edgerly (Abstr., 1900, ii, 272), is conveniently prepared by dissolving small quantities of tellurium in a slight excess of nitric acid and evaporating the solution obtained from several experiments. In this way, the separation of tellurium is reduced to a minimum. This salt, however, even after repeated crystallisation, still contains traces of silver and copper.

Tellurium can be separated from all other elements except antimony by distillation in a vacuum, and since this element is removed in purifying the basic nitrate, it follows that a combination of the two processes should lead to the production of pure tellurium. The product obtained by reducing the recrystallised nitrate with sulphur dioxide is distilled under 9—12 mm. pressure in a tube divided into segments by asbestos partitions. After repeated distillation through three or four of these compartments, a specimen is obtained which is quite free from impurities. The spectrum of this product agrees in every respect with that of the element prepared from diphenyl telluride (Steiner, Abstr., 1901, ii, 235, 236).

The foregoing method is more readily carried out and is far less wasteful than that based on fractional precipitation with sulphur dioxide.

Telluric acid,  $\text{Te}(\text{OH})_6$ , the basic sulphate,  $2\text{TeO}_2 \cdot \text{SO}_3$ , and the double chlorides with ammonium and rubidium are not suitable for the atomic weight determination, the compound finally selected being the recrystallised basic nitrate. The atomic proportions of tellurium and nitrogen were determined by decomposing the basic nitrate in a modified Dumas apparatus and estimating the nitrogen, water, and residual tellurium dioxide. In this way, three experiments gave a mean atomic weight of 126.8; the method, however, is open to objection, owing to the errors incidental to the absolute method of estimating nitrogen.

The atomic weight was finally obtained with greater accuracy by heating the pure salt and weighing the dioxide. The results of seven

determinations which were very concordant showed that tellurium, obtained by the author's process, has an atomic weight of 126.7 ( $H=1$ ) or 127.88 ( $O=16$ ). The ultra-violet spectrum seems to be the best criterion of the purity of the tellurium, and photographs of the spectra of different preparations are included in the communication.

G. T. M.

**Experiments on the Atomic Weight of Tellurium.** By GIOVANNI PELLINI (*Ber.*, 1901, **34**, 3807—3810).—To purify the tellurium, diphenyl telluride was repeatedly fractionated under diminished pressure and then converted into the dibromide, which was purified by recrystallisation from benzene and then oxidised to telluric acid. The tellurium obtained from the acid was distilled in a vacuum. For the atomic weight determinations, tellurium was in one series oxidised by nitric acid to dioxide; in another series, the dioxide was reduced to tellurium in a current of hydrogen. The mean value of six determinations in the first series was 127.65 (maximum 128.05, minimum 127.41); in the second series, the mean value of three determinations was 127.62 (maximum 128.02, minimum 127.30) when  $O=16$ .

K. J. P. O.

**Preparation of Nitrogen from Ammonium Nitrate.** By JUL. MAI (*Ber.*, 1901, **34**, 3805—3806).—On heating a mixture of glycerol (2 parts) and ammonium nitrate (1 part) at  $190^{\circ}$ , a reaction begins, which continues without further application of heat until the temperature has fallen to  $150^{\circ}$ . The gas evolved is mainly nitrogen mixed with a small quantity of carbon dioxide. The reaction begins at a lower temperature, and the gas is evolved more regularly if 2 or 3 drops of concentrated sulphuric acid are added to the mixture. The glycerol is oxidised to glyceric acid and at the same time a very small amount of pyridine bases is formed. From 10 grams of ammonium nitrate, 2690 c.c. of nitrogen were obtained instead of 2775 c.c. theoretically possible (at *N.T.P.*).

K. J. P. O.

**The Condition Diagram for Phosphonium Chloride.** By GUSTAV TAMMANN (*Arch. Néer. sci. exact. nat.*, 1901, [ii], **6**, 244—256).—The melting curve of phosphonium chloride is given by the equation:  $t = 28.5 + 0.0329(p - 50) - 0.00000366(p - 50)^2$  up to a pressure of 1550 kilos., and above this by  $t = 28.5 + 0.0295(p - 50) - 0.00000159(p - 50)^2$ . The change of volume on fusion was determined by the method already described (*Abstr.*, 1900, ii, 714); at the triple point, the change in volume amounts to 0.87 c.c. per gram, that is five times greater than the greatest (naphthalene) known up to the present. The calculated heat of fusion, 180 cal. per gram, is more than double that of water, and the high value is probably due to the fact that phosphonium chloride does not melt without dissociation. Phosphonium chloride exists at low temperatures as a white (amorphous?) mass; at higher temperatures, in clear crystals. The transition point is near  $-41^{\circ}$  and the crystals (supercooled) have the higher vapour pressure. Phosphonium chloride can be obtained in the hypercritical condition, which was found to be impossible in the case of carbon dioxide (*Abstr.*, 1899, ii, 635).

J. McC.



**Oxidation of Boron to Silica and Reduction of Boric Acid to Silicic Acid.** By FRIEDRICH FITTICA (*Chem. Zeit.*, 1901, 25, 929—930).—It is claimed that when amorphous boron is oxidised with barium peroxide, with potassium chlorate and sulphuric acid, or with other oxidising agents, considerable amounts of silica are formed, and also that when boric acid is reduced by the addition of sodium to a solution of boric acid in strong alkali or by the aid of zinc dust, silicic acid is formed. It is suggested that  $B_4 = SiO$ . J. J. S.

**The Supposed Conversion of Boron into Silica and of Boric Acid into Silicic Acid.** By CONSTANTIN COUNCLER (*Chem. Zeit.*, 1901, 25, 977—978).—A criticism on Fittica's communication (preceding abstract). J. J. S.

**Oxidation of Boron and Reduction of Boric Acid to Silicon Compounds.** By FRIEDRICH FITTICA (*Chem. Zeit.*, 1901, 25, 978).—A reply to Councler (preceding abstract). J. J. S.

**Influence of High Temperature on the Texture of the Hydrogel of Silicic Acid.** By JACOBUS M. VAN BEMMELEN (*Arch. Néer. sci. exact. nat.*, 1901, [ii], 6, 607—624. Compare Abstr., 1897, ii, 137; 1899, ii, 12, 84).—The hydrogel of silicic acid when ignited loses its power of absorbing water. Ignition for a short time causes only partial loss of this power, and the water which is then absorbed merely fills up the spaces in the network of the silica. Prolonged ignition causes the complete disappearance of these spaces, with consequent contraction of the whole mass.

The sp. gr. after ignition is 2.2; the sp. gr. of the material forming the network of the hydrogel is higher than this (2.5—3.0), which indicates that the substance expands when dehydrated. J. McC.

**Direct Conversion of Gas Carbon into Diamond.** By ALBERT LUDWIG (*Chem. Zeit.*, 1901, 25, 979—980).—Diamond crystals are formed when an electric current is passed through an iron spiral embedded in powdered gas carbon and surrounded by an atmosphere of hydrogen under great pressure. The same transformation occurs in the absence of iron, but a much higher temperature is required.

J. J. S.

**Decomposition of the Chlorides of Alkali Metals.** By C. W. VOLNEY (*J. Amer. Chem. Soc.*, 1901, 23, 820—824).—When sodium chloride (1 mol.) is treated at 18° with sulphuric acid (1 mol.) of sp. gr. 1.84, the following reaction takes place without any development of heat:  $2NaCl + 2H_2SO_4 = NaHSO_4 + H_2SO_4 + HCl + NaCl$ . On heating the residue to 120°, a further quantity of hydrogen chloride is evolved, in accordance with the equation:  $NaHSO_4 + H_2SO_4 + NaCl = 2NaHSO_4 + HCl$ . When potassium chloride is treated with concentrated sulphuric acid at 17—18°, the temperature rises to 30° and then gradually falls to 17°, whilst in the case of ammonium chloride under the same conditions the temperature rapidly falls from 18° to 1°.

E. G.

**Electrolysis of Ammonium Chloride [and Ammonium Iodide] in Solution in Liquefied Ammonia.** By HENRI MOISSAN (*Compt. rend.*, 1901, 133, 713—714. Compare Abstr., 1899, i, 410; ii, 152).—The electrolysis of ammonium chloride, bromide, and iodide in solution in carefully dried liquefied ammonia was carried out in a U-tube of glass, platinum electrodes being used (compare Ruff, Abstr., 1901, ii, 653). At  $-50^{\circ}$ , the iodide was very soluble, the bromide moderately, the chloride little, soluble, and ammonium fluoride nearly insoluble in liquefied ammonia.

Liquefied ammonia, prepared with care, is practically a non-conductor (Frenzel, Abstr., 1900, ii, 474). When ammonium chloride is dissolved in it, chlorine is evolved at the anode, and at  $-60^{\circ}$  to  $-80^{\circ}$  is free from nitrogen; at the same time, the liquid becomes yellow from the presence of dissolved chlorine; no chloride of nitrogen is produced. Pure hydrogen is evolved continuously at the cathode. In the case of a solution of ammonium iodide, iodine is deposited at the anode, and does not react with, or dissolve in, the liquid ammonia at  $-70^{\circ}$ , even after 24 hours. If the temperature is allowed to rise, the iodine crystals disappear and a very heavy, dark-coloured liquid is formed, which falls to the bottom of the tube (compare Hugot, Abstr., 1900, ii, 274).

K. J. P. O.

**Study of Ammonium Amalgam.** By HENRI MOISSAN (*Compt. rend.*, 1901, 133, 803—808).—The previous work on the existence of ammonium amalgam is discussed, and it is pointed out that the first problem is the accurate measurement of the ammonia and hydrogen evolved in the decomposition of the amalgam. To solve this problem, the author prepares the amalgam by acting on sodium amalgam with a solution of ammonium chloride (or ammonium iodide) in liquefied ammonia at  $-35^{\circ}$ ; sodium chloride (or iodide) and a metallic mass are rapidly formed; no gas is evolved. The liquid ammonia is poured off from the metal and the latter washed with liquid ammonia and finally with dry ether, saturated with hydrogen, and cooled to  $-80^{\circ}$ . At  $-80^{\circ}$ , the metal becomes very hard; at  $-40^{\circ}$ , it begins to liquefy, and at  $-30^{\circ}$  to increase in volume; at  $+15^{\circ}$ , the volume has increased twenty-five or thirty fold, and a characteristic pasty mass is formed. In the decomposition accompanying this increase in volume, heat is developed, and the temperature is raised  $5-6^{\circ}$  above the surroundings.

In order to measure the gases evolved in the decomposition, a portion of the metal, which was cooled to  $-80^{\circ}$ , was placed in a glass tube, which was then exhausted whilst the temperature was maintained between  $-80^{\circ}$  and  $-90^{\circ}$ . At this temperature, no decomposition took place during the exhaustion. The temperature was allowed to rise, and after twelve or fifteen hours, decomposition was complete. In all the experiments, the gas evolved consisted accurately of two volumes of ammonia and one of hydrogen. In some of the experiments, the cooled metal was washed with sulphuric acid or ether saturated with hydrogen chloride; although part of the amalgam was destroyed, the remainder gave up the same proportion of ammonia and hydrogen. The author, however, believes that the radicle ammonium is not present in the metal, but that an ammoniacal hydride is formed, for when an aqueous solution

of ammonia is caused to act on pasty sodium amalgam, hydrogen is slowly evolved, whilst if the amalgam contains sodium hydride, the metal immediately swells up and forms a pasty mass.

When hydrogen is passed over sodium heated at  $320^{\circ}$ , the gas is rapidly absorbed and a transparent, crystalline, hygroscopic hydride,  $\text{Na}_2\text{H}$ , is formed, which, as a powder, takes fire in air or oxygen, and in chlorine (Troost and Hautefeuille, *Abstr.*, 1874, 767). When heated in a vacuum, the hydride decomposes into sodium and hydrogen. The hydride can be readily separated from excess of metallic sodium by treating the mixture with dry liquid ammonia, when the sodium dissolves as sodium-ammonium, leaving the pure hydride. K. J. P. O.

**Decomposition of Calcium-Ammonium and of Lithium-Ammonium by Ammonium Chloride.** By HENRI MOISSAN (*Compt. rend.*, 1901, 133, 715—717. Compare *Abstr.*, 1901, ii, 600, 653).—In order to ascertain if ammonium is capable of existing at about  $-100^{\circ}$ , the author has caused calcium-ammonium ( $\text{Ca}[\text{NH}_3]_4$ ) to interact with ammonium chloride in the presence of liquefied ammonia. Pure, dry ammonia was led over a known weight of calcium contained in a U-tube, one of the arms of which was constricted. A crystal of dry ammonium chloride was placed in the constriction. On cooling the tube until the ammonia liquefied, calcium-ammonium was formed and dissolved in the excess of liquid ammonia. As more ammonia liquefied, the ammonium chloride became immersed in and dissolved by the liquid. The reddish-brown colour of the calcium-ammonium then rapidly disappeared, hydrogen gas was evolved, and collected in a special apparatus connected with the U-tube. After the evaporation of the ammonia, a compound of calcium chloride and ammonia remained in the U-tube. The volume of the hydrogen obtained showed that at the temperature used ( $-80^{\circ}$ ) ammonium does not exist. Exactly similar results were obtained when lithium was employed instead of calcium. K. J. P. O.

**Ammonium: Action of Hydrogen Sulphide on Metallo-ammonium.** By HENRI MOISSAN (*Arch. Néer. sci. exact. nat.*, 1901, [ii], 6, 490—496; and *Compt. rend.*, 1901, 33, 771—774).—After tracing the history of the searches after ammonium, the author shows that when liquid hydrogen sulphide acts on a known weight of lithium-ammonium or calcium-ammonium at between  $-75^{\circ}$  and  $-70^{\circ}$ , the sulphide of the metal is produced along with free ammonia and hydrogen, according to the equations  $(\text{LiNH}_3)_2 + \text{H}_2\text{S} = \text{Li}_2\text{S} + 2\text{NH}_3 + \text{H}_2$ , and  $\text{Ca}(\text{NH}_3)_4 \cdot 2\text{NH}_3 + \text{H}_2\text{S} = \text{CaS} + 6\text{NH}_3 + \text{H}_2$ . There is therefore no evidence of the existence of ammonium at this low temperature. Ruff's results (*Abstr.*, 1901, ii, 653) have been confirmed. J. McC.

**Solubility of Silver Bromide and Iodide in Water.** By FRIEDRICH KOHLRAUSCH and F. DOLEZALEK (*Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 1018—1023).—The determination of solubility is based on the increase in the conductivity of water shaken up with these compounds (compare Kohlrausch and Rose, *Abstr.*, 1894, ii, 7). It is found that saturated solutions of silver bromide and iodide

(at 21°) contain, respectively, 0.107 mg. and 0.0035 mg. of the salt per litre. These values are smaller than those previously obtained (*loc. cit.*), owing probably to the precautions taken, but agree fairly well with the values based on the potential differences between a silver electrode and the saturated solutions referred to (compare Danneel, *Abstr.*, 1900, ii, 467). J. C. P.

**Silver Subhaloids.** By KOLOMAN EMSZT (*Zeit. anorg. Chem.*, 1901, 28, 346—354).—Vogel claims to have prepared silver subhaloids by the action of cuprous chloride, bromide, and iodide on silver nitrate, and concludes that these are not mixtures of silver and silver haloid. Analysis leads to the formula  $\text{Ag}_4\text{Cl}_2$  for the subchloride; when the substance is treated with nitric acid, however, 2 mols. of silver are dissolved and 2 mols. of silver chloride are left, whilst ammonia or sodium thiosulphate extracts 2 mols. of silver chloride and leaves 2 mols. of silver. On continued shaking with mercury, silver is extracted. By elutriation, the composition is changed.

Light is supposed to produce on the photographic plate a subhaloid of silver which is acted on by the developer. The substances prepared from cuprous salts are themselves acted on by light and are not affected by developers. The author concludes that these supposed subhaloids are merely mixtures of silver and silver haloid produced by the reaction:  $\text{Cu}_2\text{Cl}_2 + 4\text{AgNO}_3 = 2\text{Ag} + 2\text{AgCl} + 2\text{Cu}(\text{NO}_3)_2$ . J. McC.

**The so-called Silver Peroxynitrate.** By SIMEON L. TANATAR (*Zeit. anorg. Chem.*, 1901, 28, 331—336).—The “silver peroxynitrate” was obtained by electrolysis of a 25 per cent. solution of silver nitrate between platinum electrodes at 0°, the anode and cathode being separated by a porous cylinder. The substance is deposited at the anode in dark green crystals with a metallic lustre (with 10 dichromate cells, 5 grams can be obtained in an hour). Different preparations had the same composition; the crystals are free from water (Mulder, *Abstr.*, 1896, ii, 561; 1897, ii, 260; Šulc, *Abstr.*, 1897, ii, 99) and contain 8.09 per cent. of peroxide oxygen, 79.44 of total silver, and 18.13 of silver nitrate—amounts corresponding with those required for the formula  $\text{Ag}_2\text{NO}_{11}$ . With potassium iodide, the crystals give iodine and potassium iodate.

Electrolysis of other nitrates in neutral and alkaline solutions gives nothing indicating the formation of pernitrites and there is no evidence of the production of pernitrites by the action of hydrogen peroxide on the nitrates of the alkali or alkaline earth metals.

By the electrolysis of silver fluoride, a product is obtained which very closely resembles “silver peroxynitrate.” The product, on being heated, evolves oxygen violently; it contains more peroxide oxygen than silver oxide ( $\text{Ag}_2\text{O}_2$ ). Analysis (8.3 per cent. of peroxide oxygen) leads to the formula  $\text{Ag}_{15}\text{F}_3\text{O}_{16}$ . It is highly improbable that in this compound oxygen is directly united to fluorine, and since the ratio of silver to oxygen is not 1 : 1, it is to be assumed that silver forms another peroxide besides  $\text{Ag}_2\text{O}_2$  and the salt may be a molecular compound,  $4\text{Ag}_3\text{O}_4 \cdot 3\text{AgF}$ . Analogously, “silver peroxynitrate” is  $2\text{Ag}_3\text{O}_4 \cdot \text{AgNO}_3$ .

$\text{Ag}_{15}\text{F}_3\text{O}_{16}$ , when digested on the water-bath, and washed with hot water gives the compound  $2\text{Ag}_3\text{O}_4 \cdot \text{AgF}$  (of the same type as the nitrate) with 8.94 per cent. of peroxide oxygen. J. McC.

**Solubility of Silver Sulphate and Mercurous Sulphate.** By KARL DRUCKER (*Zeit. anorg. Chem.*, 1901, **28**, 361—363).—The solubility of these sulphates in water, sulphuric acid, and potassium sulphate solutions at 25° are as follows, the solubility being expressed in grammols. per litre, and  $c$  being the concentration of the acid or salt solution used :

Mercurous sulphate.

	$c$ .	Solubility.
H <sub>2</sub> O.....	—	$11.71 \times 10^{-4}$
$\frac{1}{2}$ H <sub>2</sub> SO <sub>4</sub> .....	0.0400	$8.31 \times 10^{-4}$
$\frac{1}{2}$ H <sub>2</sub> SO <sub>4</sub> .....	0.1000	$8.78 \times 10^{-4}$
$\frac{1}{2}$ H <sub>2</sub> SO <sub>4</sub> .....	0.2000	$8.04 \times 10^{-4}$
$\frac{1}{2}$ K <sub>2</sub> SO <sub>4</sub> .....	0.2000	$9.05 \times 10^{-4}$

Silver sulphate.

H <sub>2</sub> O.....	—	$2.57 \times 10^{-2}$
$\frac{1}{2}$ H <sub>2</sub> SO <sub>4</sub> .....	0.0200	$2.60 \times 10^{-2}$
$\frac{1}{2}$ H <sub>2</sub> SO <sub>4</sub> .....	0.0400	$2.64 \times 10^{-2}$
$\frac{1}{2}$ H <sub>2</sub> SO <sub>4</sub> .....	0.1000	$2.71 \times 10^{-2}$
$\frac{1}{2}$ H <sub>2</sub> SO <sub>4</sub> .....	0.2000	$2.75 \times 10^{-2}$
$\frac{1}{2}$ K <sub>2</sub> SO <sub>4</sub> .....	0.0200	$2.46 \times 10^{-2}$
$\frac{1}{2}$ K <sub>2</sub> SO <sub>4</sub> .....	0.0400	$2.36 \times 10^{-2}$
$\frac{1}{2}$ K <sub>2</sub> SO <sub>4</sub> .....	0.1000	$2.31 \times 10^{-2}$
$\frac{1}{2}$ K <sub>2</sub> SO <sub>4</sub> .....	0.2000	$2.32 \times 10^{-2}$

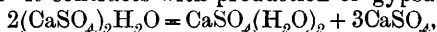
In the case of silver sulphate, the increase of solubility with increasing concentration for sulphuric acid indicates the existence of a new salt the solubility of which more than compensates for the normal isohydric depression.

J. McC.

**The Formation of Natural Anhydrite and the Rôle of Time in Chemical Transformations.** By JACOBUS H. VAN'T HOFF [with FREDERICK G. DONNAN, EDWARD F. ARMSTRONG, WILLY HINRICHSSEN, and FRITZ WEIGERT] (*Arch. Néer. sci. exact. nat.*, 1901, [ii], **6**, 471—489. Compare Abstr., 1900, ii, 531; 1901, ii, 506).—Gypsum is only very slowly transformed into the hemihydrate or into anhydrite at the transition temperature. The tension of water vapour from gypsum attains the value of one atmosphere with formation of the hemihydrate, (CaSO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O, at 101.45°; this point has been found by noting the rise of temperature produced by the addition of common salt to a mixture of gypsum and water, and then by adding water to a mixture of higher boiling point, the temperature remaining constant until, in the first case, the gypsum was completely converted into the hemihydrate, and in the second case until the hemihydrate was completely transformed into gypsum. The transition is greatly accelerated by the presence of solvent liquids; in a tensimeter containing a mixture of precipitated gypsum and the hemihydrate moistened with a solution of magnesium chloride, the tension at 50° became constant at 49.5 mm. after 7 days. At 25°, the tension is 9.1 mm. and 4.99 mm. at 17°. The connection between tension and temperature is given by the equation  $\log p = \log p' + 1.493 - 567.7/(t + 273)$ , where  $p$  is the ten-

sion of gypsum,  $p'$  that of water, both at the temperature  $t$ . When  $p = p'$  (970 mm.),  $t = 107.2^\circ$ ; this would indicate that  $2\text{CaSO}_4(\text{H}_2\text{O})_2 \rightleftharpoons (\text{CaSO}_4)_2, \text{H}_2\text{O} + 3\text{H}_2\text{O}$  takes place at this temperature, and in a dilatometer, containing moist gypsum and using mercury as indicating liquid, a change of volume has been observed at about  $107^\circ$ . In presence of a solution containing 20 per cent. of sodium chloride, gypsum commences to dehydrate at  $93^\circ$ .

For the transformation of gypsum into soluble anhydrite, neither natural nor precipitated gypsum is suitable, but gypsum obtained by treating plaster of paris with much water gave good results. The vapour tension of gypsum in forming anhydrite is higher than that when the hemihydrate is produced:  $\log p = \log p' + 1.41 - 518.8/(t + 273)$ . The transition temperature (at which  $p = p'$ ) corresponding with the reaction  $\text{CaSO}_4(\text{H}_2\text{O})_2 = \text{CaSO}_4 + 2\text{H}_2\text{O}$  is  $95^\circ$ . The hemihydrate is unstable and at  $90^\circ$  it contracts with production of gypsum,



then expands slowly owing to formation of anhydrite,  $\text{CaSO}_4(\text{H}_2\text{O})_2 = \text{CaSO}_4 + 2\text{H}_2\text{O}$ .

The formation of natural anhydrite takes place extremely slowly, but has been observed at  $37^\circ$ . The temperature of formation is depressed by the presence of sodium chloride or other salts, and in this way the natural deposits may be accounted for without assuming a high temperature at the time of formation.

Transitions, such as those referred to above, take place at very different speeds. In the case of salts, double salts, and their hydrates, if the acid is monobasic and the metal monatomic, the transformation is rapid. If the acid is dibasic or the metal diatomic, it is slower (compare supersaturation of sodium sulphate and carbonate, calcium chloride, &c.), and if the acid is dibasic and the metal di- or tri-atomic, hours, or even days, may be required for the change to take place completely (compare the very slow deposition of ferric chloride from its supersaturated solution). In the case of the non-metals, the resistance to transformation increases with the molecular magnitude (ozone and oxygen, plastic and ordinary sulphur, white and red phosphorus, the various modifications of carbon). The idea of "false equilibrium" may be in some measure accounted for by this influence of time on reaction. J. McC.

**Solubility of Gypsum in Aqueous Solutions of Sodium Chloride.** By FRANK K. CAMERON (*J. Physical Chem.*, 1901, 5, 556—576).—The solubility of gypsum is greatly increased by the addition of sodium chloride, thus, at  $26^\circ$ , the solubility per 100 grams of water is 0.2126 gram, but by the addition of 15.2 grams of sodium chloride it is increased to 0.76 gram. Below  $37.5^\circ$ , a maximum of solubility is obtained when the quantity of sodium chloride present is about 135—140 grams per litre; at higher temperatures, the existence of this maximum is doubtful. The transition temperature of the gypsum to the hemihydrate is shown to be dependent on the medium with which it is in contact; in paraffin, change does not occur until about  $145^\circ$ , although in presence of a strong sodium chloride solution it occurs at  $101.45^\circ$ . The rate of dissolution of gypsum in pure water is exceedingly slow, a fact which probably accounts for the diverse numbers which

have been given for its solubility; the author's results are, at 26°, about 1 part of gypsum in 372 parts pure water. The theoretical explanation is not fully discussed, but the author considers that the maximum point of the solubility cannot be accounted for by our present hypotheses regarding solutions.

L. M. J.

**Density and Expansion by Heat of Solutions of Magnesium Chloride.** By GUSTAV J. W. BREMER (*Arch. Néer. sci. exact. nat.*, 1901, [ii], 6, 455—470).—The densities of solutions of magnesium chloride of different concentrations have been determined at various temperatures; for the solutions examined, the density at any particular temperature can be ascertained by means of the formula  $d_t = d_0 (1 - at - bt^2)$ , the values of  $d_0$ ,  $a$ , and  $b$  being:

Grams of magnesium chloride per 100 c.c. of solution.	$d_0$ .	$a$ .	$b$ .
20.0004	1.160503	$2.2738 \times 10^{-4}$	$1.3443 \times 10^{-6}$
13.3111	1.11055	$2.0072 \times 10^{-4}$	$1.7534 \times 10^{-6}$
9.9506	1.08451	$1.8587 \times 10^{-4}$	$2.0482 \times 10^{-6}$
6.7158	1.059117	$1.7208 \times 10^{-4}$	$2.2884 \times 10^{-6}$

The density at 0°,  $d_0$ , expressed as a function of the weight of magnesium chloride,  $p$ , in 100 c.c. of solution, is  $d_0 = 1 + (9.1729 \times 10^{-3} \times p) - (5.507 \times 10^{-5} \times p)$ . The coefficient of expansion,  $a$ , increases with the concentration, whilst  $b$  diminishes, which indicates that the expansion is the more regular the higher the concentration. The curves representing the expansion of the four solutions intersect near 60°.

J. McC.

**Formation of Tachyhydrite.** By JACOBUS H. VAN'T HOFF, F. B. KENRICK, and HARRY M. DAWSON (*Zeit. physikal. Chem.*, 1901, 39, 27—63).—The solubility relations of magnesium chloride and calcium chloride were investigated and the saturation fields obtained for the compounds  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ;  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ;  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ , and tachyhydrite. Equilibrium between tachyhydrite and the two hexachlorides occurs at 22.39°, at which temperature the double salt is first deposited; at 29.4°, the hexahydrate of calcium chloride passes into the tetrahydrate, but the temperature is lowered by the addition of magnesium chloride, so that the equilibrium temperature of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ;  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ , and tachyhydrite is only 25°. A diagram is given representing the solubilities between 16.7° and 32°. Increase of pressure causes a rise of temperature of formation of tachyhydrite and by direct determination with a manocryometer the temperature coefficient was found to be +0.0162° per atmosphere. The value may be calculated by the expression  $dT/dP = 1033.3T(v_2 - v_1)/42500r$ , where  $v_2$  and  $v_1$  are respectively the specific volumes of the tachyhydrite with its saturated solution and the equivalent simple hydrates, and  $r$  is the thermal value of the change. Direct determination led to  $v_2 - v_1 = 0.06342$  c.c.; the densities were found to be,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} = 1.5907$ ;  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O} = 1.7182$ ; tachyhydrite = 1.6655, saturated solution 1.4477, and hence  $v_2 - v_1 = 0.06323$  c.c. The value of  $r$ , obtained indirectly from the

heats of solution of the various compounds, is 33.82 cal., and from these numbers, the result  $dT/dP = 0.0135^\circ$  per atmosphere is obtained, a value which agrees well with the direct determinations (see Abstr., 1900, ii, 12).  
L. M. J.

**Hydroxides of Zinc and Lead.** By W. HERZ (*Zeit. anorg. Chem.*, 1901, 28, 474–476).—Zinc hydroxide, precipitated from a solution of zinc sulphate by dilute potassium hydroxide, readily dissolves in excess of potassium hydroxide and is completely dissolved when for 1 Zn there are 6 OH groups. If, however, the zinc hydroxide is previously dried at  $60\text{--}70^\circ$  in a vacuum desiccator, it becomes comparatively difficult to dissolve, and is completely dissolved when for 1 Zn there are 35.8 OH groups in the solution. Lead hydroxide, on the other hand, is not altered in solubility by drying at  $60\text{--}70^\circ$ . It is completely dissolved when for 1 Pb there are 8.5 to 8.8 OH groups in the solution.  
E. C. R.

**Action of Water on Lead.** By STANISLAV RŮŽIČKA (*Arch. Hygiene*, 1901, 41, 23–45).—The action of water and solutions of salts on bright metallic lead was examined by placing the lead in cylinders containing the various liquids, inserting the stopper so that the cylinder contained no air, leaving the whole for 24 hours, and then estimating the amount of lead contained in the liquid. The nitrates, chlorides, sulphates, and carbonates of potassium, sodium, calcium, magnesium, and ammonium were employed, and it was found that the influence of these salts is independent of the base and that whilst nitrates increase the action of the water, or in certain concentrations leave it unaltered, chlorides, sulphates, and carbonates diminish the action, the effect increasing in the order named. When the different salts are present together, they preserve this mode of action. Thus the addition of a nitrate increases the action of solutions of chlorides, sulphates, or carbonates; the addition of a carbonate diminishes the action of solutions of nitrates, chlorides, or sulphates; the addition of a sulphate diminishes the action of solutions of nitrates or chlorides, but has no effect on those of carbonates; finally, the addition of a chloride diminishes the action of solutions of sulphates and nitrates, and either increases or leaves unaltered those of carbonates. When the same piece of lead is exposed to the action of fresh solutions containing carbonate, the amount of lead taken up diminishes very greatly and the surface of the lead becomes covered with a thin film which cannot easily be removed by rubbing.

The same diminution occurs even in the presence of nitrates and free oxygen, provided that the carbonate be present in sufficient proportion (more than half the equivalent of the nitrate). Free carbon dioxide also greatly diminishes the action of water and salt solutions on lead, both when present as a saturated solution at the commencement of the experiment, and when a current of the gas is passed through the liquid throughout the experiment. The presence of air in all cases greatly increases the solvent action.

The action of various organic substances was also examined, and it was found that infusions of grass leaves and of radish leaves diminished the action of water, whilst infusion of peat greatly increased it



The action of the salts is ascribed to the varying solubility of the lead salts of the corresponding acids, the nitrate being the most soluble and the sulphate and carbonate the least.

A. H.

**Radioactive Substances.** By FRITZ GIESEL (*Ber.*, 1901, 34, 3772—3776. Compare Abstr., 1901, ii, 99).—The assumption that radioactive lead contains a new active element is scarcely justifiable unless it can be shown that this material possesses properties differing from those of the known radioactive elements (compare Abstr., 1901, ii, 19, 159, 216, and 655).

The activity of radioactive lead sulphate, indicated either by its effect on the electroscope or by its photographic action, is not diminished on keeping, neither is it increased by the action of the cathode rays. The photographic action of the sulphate is also exhibited by the carbonate, chloride, and sulphide. The author has noticed the phosphorescence of radioactive lead sulphate, but the action is so slight that an experienced eye is required to detect it.

A sample of radioactive lead sulphate, wrapped in black paper and laid on the glass of a photographic plate, did not produce any effect even after fifteen hours; an impression was obtained, however, when the specimen was enclosed in transparent paper. This result is obtained with the sulphate and not with the corresponding chloride or sulphide.

A feebly active radium preparation enclosed in black paper affects a photographic plate when placed directly on the film; the radioactive lead sulphate enveloped in tracing paper produces an appreciable effect, even through the glass of the plate. In the former case, the Becquerel rays are operative, whilst in the latter the action is due to light rays. An artificial mixture of inactive lead and radium, containing so little of the latter substance that its presence cannot be detected by chemical means, is nevertheless distinctly radioactive, this property being noticeable in the lead sulphide and also in the iodide prepared from it.

The new product obtained by the author from the radium mother liquors (Abstr., 1901, ii, 99) resembles actinium and radium in retaining its radioactivity for a year. Polonium preparations, when preserved for a similar period, exhibit a marked diminution of activity.

The rare earths of the cerium group, containing cerium, lanthanum, and didymium as the chief constituents, give photographic impressions after 5 hours' exposure. The precipitate obtained from a thorium nitrate solution by the action of hydrogen peroxide is also strongly radioactive. In all these cases, the activity, however, rapidly diminishes, this result indicating the absence of actinium.

The water distilled off from crystallised radium-barium chloride is strongly radioactive, at first even more so than the residual chloride. That this activity is not due to any radium which might have been mechanically carried over into the distillate is shown from the fact that the action diminishes in the course of a few days.

G. T. M.

**Radioactive Substances.** By KARL A. HOFMANN and EDUARD STRAUSS (*Ber.*, 1901, 34, 3970—3973. Compare Abstr., 1901, ii, 655).—A reply to Giesel (preceding abstract). Further experiments are

described which tend to prove that the radioactive lead sulphate is free from radium, actinium, and polonium. L. L. S.

**Action of Carbon Dioxide and Alkali Salts on Metallic Oxides and the Relative Strength of Hydrochloric and Nitric Acids.** By OTTO KUHNING (*Ber.*, 1901, **34**, 3941—3945. See Abstr., 1901, ii, 656).—From a consideration of the previous experiments (*loc. cit.*), it would appear that nitric acid is a stronger acid than hydrochloric acid. Experiments are now described in which the copper oxide is replaced by mercuric oxide and lead oxide. Mercuric oxide, in the presence of sodium chloride and carbon dioxide, is slowly converted into the oxychloride,  $2\text{HgCl}_2 \cdot \text{HgO}$ , but, if the sodium chloride is replaced by sodium nitrate, the oxide is not attacked. Similar results, although not so definite, were obtained with lead oxide. R. H. P.

**Identity of the Red and Yellow Oxides of Mercury.** By J. KOSTER and S. J. STORK (*Rec. Trav. Chim.*, 1901, [ii], **20**, 394—397).—When the red oxide is finely powdered for 2 hours in an agate mortar, it is almost as easily acted on by aqueous oxalic acid as the yellow oxide, although the different action of this acid on the two oxides has hitherto been used as a pharmaceutical distinction. Obviously, as maintained by Ostwald (*Zeit. physikal. Chem.*, 1895, **13**, 159; Abstr., 1900, ii, 712), the oxides are identical and not isomeric (compare Cohen. Abstr., 1900, ii, 184, 381). W. A. D.

**Thallium Chlorobromides of the Type  $\text{Tl}_4\text{X}_6$ .** By VICTOR THOMAS (*Compt. rend.*, 1901, **133**, 735—737. Compare Abstr., 1901, ii, 159).—Cushman (Abstr., 1900, ii, 725) obtained two isomeric compounds of the formula  $\text{Tl}_4\text{Cl}_3\text{Br}_3$ , crystallising in characteristically different forms (orange plates and blood-red crystals). The author finds that the chlorobromide,  $\text{Tl}_4\text{Cl}_3\text{Br}_3$  (*loc. cit.*), crystallises usually in a mixture of needles and plates, which appear to belong to the same crystalline system. The one form readily passes into the other. Both forms, when heated alone or in presence of the solution from which they have been deposited, become blood-red; on cooling, they regain their original orange colour. K. J. P. O.

**Place of the Rare Earth Metals among the Elements.** By BERTRAM D. STEELE (*Chem. News*, 1901, **34**, 245—247).—Arguments are advanced in favour of regarding the rare earth metals as an inter-periodic group between groups IV and V of a modified periodic system with seven elements each in groups I and II, and seventeen elements in each of the groups III and IV. D. A. L.

**Metals of the Cerium Group.** By THEODOR H. BEHRENS (*Arch. Néer. sci. exact. nat.*, 1901, [ii], **6**, 67—91).—The metals of this group, lanthanum, cerium, praseodymium, neodymium, and samarium, can be separated from the metals accompanying them in minerals by precipitation as formates in slightly acid solution. If the quantity of cerium metals is small, the other metals should first be removed,

thorium as oxalate, metals of the yttrium group by precipitation with sodium sulphate, ammonium carbonate or ammonium lactate, and zirconium as lactate.

The formates of the metals of the cerium group are sparingly soluble and crystallise in the pentagonal dodecahedron form. Lanthanum and praseodymium formates are the least soluble and consequently can be separated by addition of formic acid in insufficient quantity.

The acetates are easily soluble and difficult to obtain crystallised. On boiling the solutions, basic acetates are formed. Basic lanthanum acetate with iodine turns red, then violet, and finally blue.

The oxalates are precipitated as monoclinic crystals sparingly soluble in water, but easily so in concentrated hydrochloric acid or nitric acid.

Ammonium succinate precipitates the metals of the cerium group either in spheroidal aggregates or prismatic crystals depending on the substances present in the solution. Solutions in which cerium and praseodymium nitrates predominate give flocculent masses which appear bluish in reflected light, neodymium and thorium nitrates give smooth, brown plates and spheroids. Prismatic crystals are precipitated from solutions containing much lanthanum nitrate; the crystals show brilliant polarisation colours of the second and even of the third order, and the lanthanum succinate can always be recognised amongst the other succinates. After being warmed with ammonia, cerium succinate, when moistened with hydrogen peroxide, turns brown, and can thus be distinguished from the other succinates, which remain colourless.

The metals of the cerium group can also be distinguished by conversion into benzoates or salicylates.

It is possible to obtain cerium pure by repeated crystallisation of the ammonium double nitrates; pure neodymium can only be prepared in this way with the aid of some precipitant, and on account of the isomorphous nature of the double nitrates it is not possible to separate pure praseodymium. No separation of lanthanum and praseodymium can be attained by crystallisation of the acetates.

A pure solution of lanthanum can be obtained by extracting the mixed "cerite" oxide with nitric acid of sp. gr. 1.2 for 10 minutes; even better results are obtained with dilute sulphuric acid.

When cerium is precipitated with an oxidising agent (sodium hypochlorite, hydrogen peroxide, potassium permanganate) in presence of sodium acetate, lanthanum is constantly carried down with it, and if persulphuric acid is used, the cerium precipitate is further contaminated with double sulphates of calcium and the metals of the cerium group.

By the addition of ammonia, samarium is first precipitated, then neodymium, praseodymium, and lanthanum, but no satisfactory separation can be made on this basis. Cerium nitrate, when boiled with much water, is precipitated as basic nitrate, but the precipitate constantly contains very appreciable quantities of lanthanum, samarium, and neodymium. In the same way, basic cerium sulphate can be obtained, and if care be taken that some free sulphuric acid is present, so that the cerium is not completely removed in the precipitate, an almost pure cerium salt is obtained.

Mosander's method of separating lanthanum, neodymium, and praseodymium as normal sulphates does not lead to pure products, neither does Delafontaine's modification in which the solution is shaken with alcohol.

The author does not regard it as yet possible to give a satisfactory method of separating the metals of this group in a pure form.

J. McC.

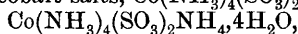
**Mechanism of Action of Hydrogen Peroxide on Permanganic Acid.** By A. BACH (*Ber.*, 1901, **34**, 3851—3855).—Traube has suggested that the reduction of permanganic acid by hydrogen peroxide is due to the readiness with which the hydrogen of the peroxide is oxidised; Berthelot, on the other hand, has suggested that the peroxide first becomes oxidised to the higher oxide,  $H_2O_3$ , which then decomposes into water and oxygen. In order to test these views, the behaviour of ethyl hydrogen peroxide towards permanganic acid and of 'Caro's acid' towards permanganic oxide were studied; it is suggested that on Traube's hypothesis these compounds should only reduce half as much oxygen as the equivalent of hydrogen peroxide, whilst on Berthelot's hypothesis the reducing power should be the same. Actually, the ethyl hydrogen peroxide behaves exactly like hydrogen peroxide, whilst Caro's acid shows a somewhat lower reducing power, and this is regarded as affording support to Berthelot's hypothesis.

T. M. L.

**Passive Iron.** By ALEXIS FINKELSTEIN (*Zeit. physikal. Chem.*, 1901, **39**, 91—110).—Determinations of the polarisation capacity and resistance of passive iron indicate that it cannot be covered by a coating of badly conducting oxide, and the numbers are very nearly equal to those obtained for platinum. Passive iron does not behave as an iron electrode, but as an oxygen electrode of variable oxygen concentration. The *E.M.F.* of iron electrodes against various solutions were determined; addition of potassium cyanide to the solutions greatly lowers the *E.M.F.*, and in solutions of mixed ferrous and ferric salts the *E.M.F.* decreases as the ferrous salt becomes replaced by ferric. The polarisation curves were investigated, and the non-existence of an oxide layer again indicated. The author discusses the cause of the passivity, and shows that it may be accounted for by the assumption that the surface of passive iron consists solely of tervalent iron, the formation of passive iron by oxidising agents and electrolysis being due to the replacement of the bivalent by tervalent iron.

L. M. J.

**Isomerism in the Cobalt-tetrammine Series.** By KARL A. HOFMANN and A. JENNY (*Ber.*, 1901, **34**, 3855—3873).—Two isomeric disulphitetetramminecobalt salts,  $Co(NH_3)_4(SO_3)_2NH_4 \cdot 3H_2O$  and



result from the action of sulphurous acid on the carbonatotetrammine chloride, or on a solution, oxidised by exposure to air, of ammoniacal cobalt acetate. The first of these has already been described (Hofmann and Reinsch, *Abstr.*, 1898, ii, 377), but it has since been found that all the water can be driven off without destroying the compound, and its formula must therefore be written in the form given above.

It forms brown, birefringent prisms belonging to the monoclinic system [ $a : b : c = 0.859 : 1 : 0.534$ ;  $\beta = 111^{\circ}23'$ ]; it affords no coloration with ammoniacal sodium nitroprusside, and no precipitate with mercurous nitrate, but slowly gives a flocculent precipitate with thallium nitrate; in aqueous solution, it has half the normal mol. weight and is regarded as dissociating into the ions  $\text{NH}_4$  and  $\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2$ . When dissolved in sulphuric acid, hydrochloric acid precipitates the praseo-chloride,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}, \text{H}_2\text{O}$ .

The second salt crystallises from water in reddish-yellow prisms which are fairly stable in air but rapidly effloresce in a vacuum; like the preceding salt, it is readily converted into the praseo-chloride, and behaves in a similar manner with thallium nitrate, mercurous nitrate, and ammoniacal nitroprusside.

These two isomeric salts cannot be regarded as merely polymorphous forms of one salt, as they give different colour reactions with sulphuric acid and are not converted into one another by recrystallisation.

The two corresponding sodium salts usually crystallise with  $2\text{H}_2\text{O}$  and  $4\text{H}_2\text{O}$  respectively. The first salt is brown in colour and has already been described (Hofmann and Reinsch, *loc. cit.*; Werner and Gröger, *Abstr.*, 1898, ii, 379); it forms square tablets, probably belonging to the monoclinic system, and is precipitated unchanged from a concentrated aqueous solution on adding alcohol, but separates from a dilute solution in reddish-brown, orthorhombic needles with  $3\text{H}_2\text{O}$ ; in aqueous solution, it shows half the normal mol. weight.

The isomeric sodium salt forms golden-yellow needles of the formula  $\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2\text{Na}, 4\text{H}_2\text{O}$ , readily effloresces, and loses all its water in a vacuum.

The salt  $\text{Co}_2(\text{NH}_3)_4(\text{SO}_3)_3, 6\text{H}_2\text{O}$  is prepared from a bye-product obtained in making the ammonium salts described above; it forms birefringent prisms, and is completely dehydrated at  $85^{\circ}$ ; when dissolved in sulphuric acid and mixed with hydrochloric acid, it gives chloropentamminocobalt chloride (purpureo-chloride),  $\text{CoCl}(\text{NH}_3)_5\text{Cl}_2$ , and is therefore regarded as a double salt of a pentammine sulphite with a triammine sulphite.

Complex salts of the formulae  $\text{Co}_3(\text{NH}_3)_8(\text{SO}_3)_6\text{Na}_3, 6\text{H}_2\text{O}$  and  $\text{Co}_3(\text{NH}_3)_6(\text{SO}_3)_6\text{Na}_2, 6\text{H}_2\text{O}$  are described.

The acid sulphite,  $\text{Co}(\text{NH}_3)_4(\text{CO}_3) \cdot \text{SO}_3\text{H}$ , forms violet-red crystals, and is shown to be a true tetrammine by its conversion into the praseo-chloride.

Three sulphito-compounds containing  $\frac{5}{3}$  mols. of  $\text{NH}_3$  are described: a dark-brown salt,  $\text{Co}_2(\text{NH}_3)_6(\text{SO}_3)_3, 3\text{H}_2\text{O}$ , crystallising in prisms; a dark-brown salt,  $\text{Co}(\text{NH}_3)_3(\text{SO}_3)_2 \cdot \text{H}_2\text{H}_2\text{O}$ , crystallising in hexagonal tablets, and a dark-brown sodium salt,  $\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})(\text{SO}_3)_2\text{Na}, 2\text{H}_2\text{O}$ , which will only part with  $2\text{H}_2\text{O}$  without decomposition. T. M. L.

**Some Allotropic Modifications of Inorganic Compounds.** By W. HERZ (*Zeit. anorg. Chem.*, 1901, 28, 342—345. Compare *Abstr.*, 1900, ii, 728; 1901, ii, 513).—Nickel sulphide, precipitated with ammonium sulphide, shows the same phenomena as cobalt sulphide. The nickel sulphide, exposed to the air, oxidises very readily to sulphate.

Chromium hydroxide, precipitated by alkali, is easily soluble in excess of the reagent; after being dried in a vacuum, however, the hydroxide is insoluble in alkalis. In these cases, the less stable form is first produced and gradually changes to the more stable form.

Zinc oxide heated to  $250^{\circ}$  shows a faint yellow colour and if the yellow (hot) and the white (cold) oxide were allotropic forms it would be expected that on prolonged heating at this temperature the change to the yellow modification would be complete. The intensity of the colour does not, however, increase, indicating that there is no transition and that the two forms cannot be considered as allotropic modifications.

J. MCC.

**Chromium Halogen Compounds with Alcohol.** By IWAN KOPPEL (*Zeit. anorg. Chem.*, 1901, **28**, 461—473).—The salt  $\text{CrCl}_3 \cdot 3\text{EtOH}$  is obtained by treating metallic chromium with a concentrated solution of dry hydrogen chloride in absolute alcohol. It crystallises in deep red needles, is fairly stable in dry air, in damp air is quickly converted into green chromium trichloride hexahydrate, and when heated yields alcohol and ethyl chloride. It dissolves in water to a red solution which quickly turns green, the same colour phenomenon taking place more slowly in alcohol, chloroform, or acetone solution. An examination of the electrical conductivity of the solution in absolute alcohol shows that this colour change is due to causes similar to that observed by Werner and Gubser (*Abstr.*, 1901, ii, 453) in the case of the green chromium chloride, the change of colour from red into green being accompanied by an increase in the electrical conductivity. This salt is also obtained by heating the violet chromium chloride with absolute alcohol and a stick of metallic zinc.

The corresponding chromium bromide salt, obtained in a similar manner, crystallises in dark reddish-brown crystals which give brown solutions that quickly turn green. It was not, however, obtained in a pure state.

E. C. R.

**Silicomolybdates.** By WLADISLAW ASCH (*Zeit. anorg. Chem.*, 1901, **28**, 273—313).—Molybdic acid, when added to a boiling solution of sodium silicate ( $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ) dissolves readily at first and some gelatinous silicic acid is separated. By further addition of molybdic acid to the saturation point, the silicic acid redissolves and the solution (which becomes intensely yellow) when evaporated at  $45^{\circ}$  deposits yellow crystals of sodium silicomolybdate,  $2\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{MoO}_3 \cdot 21\text{H}_2\text{O}$ . This salt is dimorphous. Attempts to obtain any other sodium silicomolybdate proved futile. Solutions of sodium silicomolybdate with solutions of salts of potassium, ammonium, rubidium, cesium, thallium, barium, strontium, calcium, nickel, cobalt, cadmium, aniline, pyridine, and quinoline give corresponding silicomolybdates. Of these, only the following have been analysed:  $2\text{K}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{MoO}_3 \cdot 16\text{H}_2\text{O}$ ;  $2\text{MgO} \cdot \text{SiO}_2 \cdot 12\text{MoO}_3 \cdot 30\text{H}_2\text{O}$ ;  $2\text{BaO} \cdot \text{SiO}_2 \cdot 12\text{MoO}_3 \cdot 24\text{H}_2\text{O}$ , and  $2\text{CaO} \cdot \text{SiO}_2 \cdot 12\text{MoO}_3 \cdot 24\text{H}_2\text{O}$ . With a dilute solution of silver nitrate, sodium silicomolybdate gives a small quantity of ruby crystals and a yellow salt having the composition  $2\text{Ag}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{MoO}_3 \cdot 12\text{H}_2\text{O}$ .

With concentrated silver nitrate, a yellow precipitate of  $4\text{Ag}_2\text{O}, \text{SiO}_2, 12\text{MoO}_3, 15\text{H}_2\text{O}$  is obtained.

By treating the sodium or potassium salt (1 mol.) with hydrochloric acid (4 to 8 mols.) compounds of the formulæ  $1\frac{1}{2}\text{Na}_2\text{O}, \text{SiO}_2, 12\text{MoO}_3, 17\text{H}_2\text{O}$  and  $1\frac{1}{2}\text{K}_2\text{O}, \text{SiO}_2, 12\text{MoO}_3, 14\text{H}_2\text{O}$  are formed, and these salts can also be prepared by adding the calculated quantity of alkali to the free acid. This potassium salt gives, with silver nitrate, yellow crystals of  $1\frac{1}{2}\text{Ag}_2\text{O}, \text{SiO}_2, 12\text{MoO}_3, 11\text{H}_2\text{O}$ , as well as ruby crystals which have not been analysed. With alkali or sodium carbonate, sodium silicomolybdate (with  $1\frac{1}{2}\text{Na}_2\text{O}$ ) gives only sodium trimolybdate. Silicomolybdic acid,  $\text{SiO}_2, 12\text{MoO}_3, 32\text{H}_2\text{O}$  (or  $2\text{H}_2\text{O}, \text{SiO}_2, 12\text{MoO}_3, 30\text{H}_2\text{O}$ ), was obtained by decomposing the sodium salt with dilute sulphuric acid and extracting with ether.

By dialysing a 5 percent. solution of the salt  $2\text{K}_2\text{O}, \text{SiO}_2, 12\text{MoO}_3, 16\text{H}_2\text{O}$  it was found that the ratio of  $\text{K}_2\text{O} : \text{SiO}_2 : \text{MoO}_3$  was the same in the diffused solution as in the original, indicating that the silicic and molybdic acids form a complex ion. The conductivities and densities of solutions of the acid and of the potassium salt have been determined at  $10^\circ$ ,  $20^\circ$ ,  $30^\circ$ , and  $40^\circ$ . The results indicate that the silicomolybdates are fairly stable and only suffer decomposition at high dilution, and that this decomposition is increased by rise of temperature.

By measuring the depression of the freezing point of Glauber's salt (Lowenherz, Abstr., 1896, ii, 149), caused by the addition of the sodium salt, it was found that the mol. weight corresponds with that required for the formula  $\text{Na}_4\text{SiMo}_{12}\text{O}_{40}$ . The salts  $2\text{R}_2\text{O}, \text{SiO}_2, 12\text{MoO}_3, \text{aq}$  are to be regarded as normal salts of tetrabasic silicomolybdic acid, whilst the salts  $1\frac{1}{2}\text{R}_2\text{O}, \text{SiO}_2, 12\text{MoO}_3, \text{aq}$  are acid salts of the same acid ( $\frac{1}{2}\text{R}_2\text{O}$  being replaced by  $\frac{1}{2}\text{H}_2\text{O}$ ).

At  $100^\circ$ ,  $2\text{Na}_2\text{O}, \text{SiO}_2, 12\text{MoO}_3, 21\text{H}_2\text{O}$  loses  $17\frac{1}{2}$  mols. of water, and  $1\frac{1}{2}\text{Na}_2\text{O}, \text{SiO}_2, 12\text{MoO}_3, 17\text{H}_2\text{O}$  loses 13 mols.; that is, the normal salt has  $3\frac{1}{2}$  mols. of water of constitution and the acid salt has 4.

In the analysis of the compounds the silica was determined after removing the molybdic acid by heating to a high temperature in a current of hydrogen chloride. J. McC.

**Uranous Sulphate.** By WILLIAM OECHSNER DE CONINCK (*Bull. Acad. Roy. Belg.*, 1901, 483—485).—The sp. gr. of aqueous solutions of uranous sulphate as well as of solutions in sulphuric acid and hydrochloric acid have been determined. A 1 per cent. solution in water has a sp. gr. 1.0058, a 10 per cent. solution 1.0539. A 1 per cent. solution in sulphuric acid of sp. gr. 1.14 has a sp. gr. 1.1442, a 5 per cent. solution 1.1626. In solution in hydrochloric acid of sp. gr. 1.046, a 1 per cent. solution has a sp. gr. 1.0525, a 5 per cent. solution 1.0744. Water acts on uranous sulphate, producing a basic salt and a substance of the formula  $2\text{USO}_4, 3\text{UO}, 4\text{H}_2\text{O}$  has been isolated.

J. McC.

**Tin-Aluminium Alloys.** By LÉON GUILLET (*Compt. rend.*, 1901, 133, 935—937).—The action of stannic oxide on aluminium is very energetic, but the limit of inflammation is reached with a mixture corresponding with  $\text{Al}_4\text{Sn}$ . The product from this mixture, when

treated with dilute hydrochloric acid, yields lamellar and filiform crystals of the compound  $\text{Al}_4\text{Sn}$ . Similarly, mixtures corresponding with  $\text{Sn}_4\text{Al}$ ,  $\text{SnAl}$ , and  $\text{SnAl}_2$  yield lamellar and filiform crystals of the compound  $\text{AlSn}$ .  
C. H. B.

**New Element associated with Thorium.** By CHARLES BASKERVILLE (*J. Amer. Chem. Soc.*, 1901, 23, 761—774. Compare Brauner, *Proc.*, 1901, 17, 67).—Freshly precipitated thorium hydroxide was dissolved in hydrochloric acid; the solution was neutralised with ammonia and saturated with sulphur dioxide. A basic sulphite separated, and on addition of ammonia to the filtrate a further precipitate was obtained. Each of these precipitates was carefully ignited; the resulting oxides had the sp. gr. 9.38 and 10.367 respectively.

On heating a solution of thorium hydroxide in saturated citric acid solution, a white, amorphous precipitate of the hydrated citrate of real thorium was obtained, which yielded specimens of the oxide of sp. gr. varying from 9.188 to 9.253, whilst the citrate obtained by concentrating the filtrate furnished an oxide of sp. gr. 10.50. After the removal of the insoluble citrate from a large quantity of the saturated citrate solution, the filtrate slowly deposited a small quantity of heavy crystals which, on ignition, yielded 31.61 per cent. of oxide of sp. gr. 8.47—8.77; the author suggests this may be the oxide of the new metal discovered by Hofmann and Prandtl (*Abstr.*, 1901, ii, 387) in euxenite; on evaporation of the filtrate, several fractions of the crystalline citrate were obtained, the oxide from which had a sp. gr. 10.14—11.26.

The radioactivity of the oxide (sp. gr. 9.25) obtained from the insoluble citrate is very slight, whilst the oxides of high specific gravity are quite active, the activity increasing with the sp. gr.

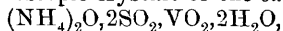
These experiments indicate the presence of a new element, the oxide of which has a high sp. gr.; its atomic weight (calculated for a quadrivalent element) appears to lie between 260 and 280. The author proposes for this metal the name *carolinium*.

The atomic weight of thorium, obtained by analysis of the tetrachloride, was found as the mean of two experiments to be 222—223.3.

E. G.

**Sulphites and Sulphates of Quadrivalent Vanadium.** By IWAN KOPPEL and E. C. BEHRENDT (*Ber.*, 1901, 34, 3929—3936).—Vanadyl sulphite forms two series of double salts with the sulphites of the alkalis, the salts of one series being blue, and having the empirical formula,  $\text{R}'_2\text{O}, 2\text{SO}_2, 3\text{VO}_2, \text{aq}$ , those of the other being green, with the formula  $\text{R}'_2\text{O}, 2\text{SO}_2, \text{VO}_2, \text{aq}$ .

The *salt*,  $(\text{NH}_4)_2\text{O}, 2\text{SO}_2, 3\text{VO}_2, \text{H}_2\text{O}$ , obtained when a solution of ammonium metavanadate (1 mol.) and ammonia (1 mol.) is saturated with sulphur dioxide and evaporated in the presence of the same gas, crystallises in long, blue, rectangular tablets, which are quite stable in air. When a saturated solution of ammonium metavanadate is mixed with a large excess of a neutral solution of ammonium sulphite and evaporated, green, microscopic crystals of the *salt*,

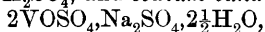


are obtained.



The corresponding potassium and sodium salts are obtained by analogous methods. The blue *potassium* salt crystallises in microscopic tablets, which dissolve in water without decomposition; the green *potassium* salt crystallises, with  $5\frac{1}{2}\text{H}_2\text{O}$ , from water in rectangular tablets, and is stable in air. The blue *sodium* salt was obtained in long, prismatic crystals with  $4\text{H}_2\text{O}$ , and the green *sodium* salt with  $5\text{H}_2\text{O}$  as a microcrystalline powder, both, however, decomposing when kept in air.

When barium metavanadate suspended in water is reduced with sulphur dioxide, a solution is obtained which, when evaporated in the presence of sulphur dioxide, deposits a dark brown, microcrystalline powder having the composition  $3\text{VO}_2, 2\text{SO}_2, 4\frac{1}{2}\text{H}_2\text{O}$ ; this may be either vanadyl sulphite or vanadyl sulphurous acid. Double sulphates of the alkalis and vanadyl can be obtained by crystallisation of the mixed sulphates at  $100^\circ$  or above from solutions containing sulphuric acid. *Ammonium vanadyl sulphate*,  $2\text{VOSO}_4, (\text{NH}_4)_2\text{SO}_4, \text{H}_2\text{O}$ , *potassium vanadyl sulphate*,  $2\text{VOSO}_4, \text{K}_2\text{SO}_4$ , and *sodium vanadyl sulphate*,



were obtained as extremely hygroscopic, microcrystalline tablets. An *ammonium vanadyl sulphate* of the composition  $(\text{NH}_4)_2\text{SO}_4, \text{VOSO}_4, 3\frac{1}{2}\text{H}_2\text{O}$ , was also prepared.

R. H. P.

**Compounds of Gold and Chlorine.** By FERNAND MEYER (*Compt. rend.*, 1901, 133, 815—818).—If gold is treated with liquid chlorine in a sealed tube at the ordinary temperature, the metal is superficially attacked and converted into a crystalline, red mass. When the tubes containing the gold and chlorine are heated intermittently at  $100^\circ$ , the gold entirely dissolves, forming a deep yellow solution, and, on cooling, auric chloride separates in wine-red, very hygroscopic crystals.

The dissociation of auric chloride has been studied in a specially constructed apparatus. At  $150^\circ$ , the dissociation becomes marked, and a greyish-green solid (a mixture of aurous chloride and gold) and chlorine are formed. The dissociation pressure was measured up to  $205^\circ$ , when the system ceases to have only one variable, as the auric chloride begins to volatilise. If at a given temperature,  $t$ , the chlorine (which was at a given pressure,  $p$ ) was slowly removed from the apparatus, until all the auric chloride had disappeared, the pressure assumed a new value,  $p'$ , which remained constant until only gold was left in the tube. Auric chloride, therefore, dissociates into aurous chloride and chlorine. Aurous chloride is sensibly dissociated at  $170^\circ$ ; the dissociation pressure was measured up to  $240^\circ$ . These experiments show that there is only one compound of gold and chlorine, namely, aurous chloride, containing less chlorine than auric chloride.

K. J. P. O.

**Ruthenium. IV. The Chlorides.** By JAS. LEWIS HOWE (*J. Amer. Chem. Soc.*, 1901, 23, 775—788).—*Cæsium* and *rubidium ruthenichlorides*,  $\text{Cs}_2\text{RuCl}_6$  and  $\text{Rb}_2\text{RuCl}_6$ , crystallise in black, almost opaque, regular octahedra and are slightly soluble in water. The *oxyruthenichlorides*,  $\text{Cs}_2\text{RuO}_2\text{Cl}_4$  and  $\text{Rb}_2\text{RuO}_2\text{Cl}_4$ , form dark purple, cubic crystals, and are instantly decomposed by water with production of a black precipitate. *Cæsium* and *rubidium chlorides* unite with

ruthenium trichloride to form the *double* salts,  $\text{Cs}_2\text{RuCl}_5\cdot\text{H}_2\text{O}$  and  $\text{Rb}_2\text{RuCl}_5\cdot\text{H}_2\text{O}$ , which are dark brown powders fairly soluble in water.

When a slightly acid solution of caesium ruthenichloride is heated with water and alcohol, a rose-coloured *salt*,  $2\text{CsCl}\cdot\text{Ru}(\text{OH}_2)\text{Cl}_3$ , is produced, which crystallises in prisms and is very slightly soluble in water. By electrolytic reduction of ruthenium trichloride and addition of caesium chloride to the product, a bluish-green *substance*,  $3\text{CsCl}\cdot 2\text{RuCl}_2\cdot\text{H}_2\text{O}$ , is precipitated which rapidly oxidises in the air.

E. G.

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## Mineralogical Chemistry.

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**Formation of Coal.** By S. STEIN (*Chem. Centr.*, 1901, ii, 950 ; from *Magy. chem. folyóirat*, 6, 39—42).—Wood was heated with water in sealed tubes, as in the experiments of Cagniard de la Tour, and black masses resembling coal obtained ; these gave the following results on analysis :

Temperature.	Time.	H per cent.	C per cent.
245°	9 hours	5·4	64·30
250	6 „	5·1	69·20
255	6 „	5·2	70·3
265	5 „	4·7	72·8
275	6 „	4·5	74·0
280	5 „	4·1	77·6
290	5 „	3·8	81·3

The increase in the amount of carbon depends on the pressure as well as on the temperature and duration of the experiment, since at atmospheric pressure for 2 days at a red heat the amount of carbon never exceeded 78 per cent.  
L. J. S.

**A Variety of Polydymite or Sychnodymite.** By WILH. STAHL (*Zeit. Kryst. Min.*, 1901, 35, 289 ; from *Berg-u. hüttenm. Zeit.*, 1899, 58, 182).—Light to dark grey, cubic crystals from the Siegthal gave on analysis :

Cu.	Ni.	Co.	Fe.	S.	Insol.	Total.
23·46	5·70	26·80	3·86	39·28	0·47	99·57.

This gives the same general formula  $(\text{Co}, \text{Cu}, \text{Ni}, \text{Fe})_4\text{S}_5$ , as both polydymite and sychnodymite, and approaches the latter in the proportions in which the metals are present.  
L. J. S.

**Pyrites and Marcasite.** By HENRY N. STOKES (*Bull. U.S. Geol. Survey*, 1901, No. 186 [*Ser. E., Chem. & Physics*, No. 35], 1—50).—When pyrites and marcasite are not distinctly crystallised it is often

difficult to distinguish between them, and the characters usually relied on for this purpose, namely, colour, sp. gr. and ease of oxidation, are not altogether trustworthy. It is pointed out that the true colour of marcasite is tin-white, the usual bronze-yellow being due to tarnish. The author has devised a chemical method for the discrimination of these minerals, and for their quantitative determination in mixtures. This method depends on the fact that when pyrites or marcasite is boiled with an excess of a solution of a ferric salt until the latter is completely reduced, the ratio of sulphur oxidised to mineral decomposed is perfectly definite and characteristic of each mineral, provided certain standard and easily controllable conditions are observed. With a boiling solution of iron ammonium alum containing 1 gram of ferric iron and 16 c.c. of 25 per cent. free sulphuric acid per litre, the percentage of sulphur oxidised in pyrites is about 60·4, and in marcasite about 18 per cent. of the total sulphur. These figures are the characteristic oxidation coefficients, which depend, however, on the temperature and concentration of the solution. The oxidation of pyrites or marcasite to ferrous salt, sulphuric acid and free sulphur cannot be expressed by any single equation, but takes place according to two or more. An empirical curve for the oxidation coefficients of mixtures of pyrites and marcasite in known proportions gives a means of quantitatively determining the composition of naturally occurring mixtures of these minerals. The influence of various impurities on the results is described: the nature of the impurities can sometimes be distinguished by this method, for example, whether chalcopyrite or bornite is present in cuprififerous pyrites. The determinations are made in an atmosphere of carbon dioxide, and a detailed description is given of the apparatus employed.

Some of the experiments which have been made (Abstr., 1895, ii, 316; 1896, ii, 108; 1898, ii, 602; 1901, ii, 319) with the view of determining the state of combination or valency of iron in pyrites, &c., are here repeated, only to show that the evidence derived from such experiments is inconclusive. L. J. S.

**Hydrogöthite, a Definite Hydrated Iron Oxide.** By J. SAMOILOFF (*Zeit. Kryst. Min.*, 1901, 35, 272—274).—In 1889, P. A. Zemjatschensky described as a new mineral, under the name hydrogöthite, a hydrated iron oxide with the formula  $3\text{Fe}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ ; it was found as thin veins in limonite in central Russia, and had a fibrous structure and cochineal-red colour. These observations, which have not been generally accepted, are confirmed by the present author, who considers hydrogöthite to be a definite mineral species; and he records its occurrence in the iron-ores of several localities in the Tula government. It occurs as thin veins in, and as crusts 2—5 mm. thick on, massive limonite, and also as a later formation in the interior of hollow limonite concretions. Analysis gave:  $\text{H}_2\text{O}$ , 12·33—13·16;  $\text{Fe}_2\text{O}_3$ , 86·01 per cent., agreeing with the above formula: phosphorus, aluminium and traces of manganese are also present. The observed sp. gr., 3·73, is probably too low. The powder of the mineral is tile-red in colour.  $\text{H} = 4$ . Under the microscope are seen transparent plates

or needles with a distinct cleavage in one direction, straight extinction, optically positive in the direction of the length, and very strong pleochroism.

L. J. S.

**Ktypeite and Conchite.** By HEINRICH VATER (*Zeit. Kryst. Min.*, 1901, 35, 149—178).—Conchite (Abstr., 1901, ii., 168, 395) is identical with aragonite, and the same is probably also true of ktypeite (Abstr., 1898, ii, 604).

L. J. S.

**Analyses of Magnesite [and Dolomite].** By JOZSEF LOCZKA (*Zeit. Kryst. Min.*, 1901, 35, 282).—The following analyses are given of: I, grey magnesite, and II, white dolomite, both from Jolsva, Gömör Co., Hungary:

	MgO.	CaO.	MnO.	FeO.	Fe <sub>2</sub> O <sub>3</sub> .	CO <sub>2</sub> .	FeS <sub>2</sub> .	Insol.	Total.
I.	44·63	—	0·16	3·88	trace	51·34	0·19	0·04	100·24
II.	21·10	30·28	trace	0·98	trace	47·61	—	0·04	100·01

L. J. S.

**Pseudogaylussite.** By CHARLES O. TRECHMANN (*Zeit. Kryst. Min.*, 1901, 35, 283—285. Compare Abstr., 1898, ii, 80).—A description, with photographic reproductions, is given of some crystals dredged up from the Clyde at Cardross opposite Greenock. They are of a reddish-brown colour, with curved faces and rounded pyramidal terminations; in cross-section they are square or rhomb-shaped. Sp. gr. 2·575 and 2·602, but the material is slightly porous. Thin sections under the microscope show the material to consist mainly of minute (0·165 mm. diam.) spherules of calcite with radially fibrous structure. Analysis gave:

Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .	CaCO <sub>3</sub> .	MgCO <sub>3</sub> .	Total.
5·52	83·52	9·03	98·07

Traces of silica, iron, manganese, chlorine, sulphuric anhydride and organic matter are also present. No new light is thrown on the origin of these peculiar pseudomorphs, which are also known by the names thinolite and jarrowite.

L. J. S.

**Artificial Preparation of Monetite.** By AUGUST DE SCHULTEN (*Chem. Centr.*, 1901, ii. 1128; from *Bull. Soc. franç. Min.*, 24, 323—326).—Crystals of anhydrous dicalcium phosphate or monetite have been prepared by slowly dropping a 0·6 per cent. solution of ammonia into a solution containing 70 grams of anhydrous calcium chloride, 226 grams of disodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>, 12H<sub>2</sub>O) in 500 c.c. of water and 80 c.c. of hydrochloric acid of sp. gr. 1·19. After remaining 2—3 weeks, dicalcium phosphate was found to have crystallised in transparent, triclinic plates [ $a : b : c = 1·049 : 1 : 1·044$ ] having a sp. gr. 2·928 at 15°. This preparation resembles, and may possibly be identical with, Kloos' martinite, Ca<sub>3</sub>H<sub>2</sub>(PO<sub>4</sub>)<sub>4</sub>· $\frac{1}{2}$ H<sub>2</sub>O which has a sp. gr. 2·894.

E. W. W.

**Stilbite and Foresite from the Elba Granite.** By ERNESTO MANASSE (*Jahrb. Min.*, 1901, ii, Ref. 28—31; *Atti Soc. Toscana Sci. Nat. Mem.*, 1900, 17, 203—227).—Stilbite occurs as a yellowish-white mass encrusting the tourmaline and other minerals in drusy cavities in the Elba granite. Analysis I is of radial aggregates of small crystals, and II of globular and sheaf shaped groups; in both cases, details are given of the amounts of water expelled at various temperatures. The first of these analyses agrees with the usual stilbite formula, which, according to Clarke's theory of the silicates (Abstr., 1897, ii, 50), is written as  $[\text{Al}(\text{SiO}_4)_3\text{AlH}_5]\text{Ca}[\text{Al}(\text{Si}_3\text{O}_8)_3\text{CaH}_3\text{Al}], 8\text{H}_2\text{O}$ . This is referred to as typical stilbite. The second analysis with more silica requires one of the  $(\text{SiO}_4)$  groups in this formula, to be replaced by the group  $(\text{Si}_3\text{O}_8)$ , whilst in an earlier analysis by Grattarola and Sansoni with less silica, there are only two  $(\text{Si}_3\text{O}_8)$  groups:

	H <sub>2</sub> O.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Total.
I.	17.75	56.59	17.73	7.03	1.73	—	100.83
II.	14.94	61.51	15.01	6.74	1.91	—	100.11
III.	16.66	48.93	27.56	5.16	1.14	trace	99.45

Foresite occurs like the stilbite, but is snow-white. It gave on analysis the results under III, agreeing with those required for the formula  $13\text{H}_2\text{O}, 12\text{SiO}_2, 4\text{Al}_2\text{O}_3, 2(\text{Ca}, \text{Na}_2)\text{O}$ , which is written in conformity with Clarke's structural formula of stilbite by replacing  $\text{H}_4$  by four  $\text{Al}(\text{OH})_4$  groups.

In discussing the origin of these zeolites, the following analyses are given of the Elba granite. I (also traces of  $\text{MnO}$  and  $\text{ZrO}_2$ ) of the normal biotite-granite; II (also trace of  $\text{MnO}$ ) of dark, fine-grained patches in the same; III, (also trace of  $\text{B}_2\text{O}_3$ ) of white veins containing the tourmaline druses:

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	<u>FeO<sub>3</sub></u> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .	H <sub>2</sub> O.	Total.
I.	69.92	15.68	4.57	1.85	0.92	3.18	4.35	0.24	0.59	101.30	
II.	70.21	15.72	5.03	2.11	1.07	3.25	3.66	0.29	0.48	101.82	
III.	75.17	14.05	0.21	0.32	0.16	4.57	5.00	—	0.45	99.93	

The orthoclase of this granite has the following composition; I, for the fresh material, II, for the slightly altered, and III, for the much altered material; whilst IV gives the composition of a zeolitic mixture representing a still further stage in the alteration of the feldspar:

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	64.85	18.14	—	0.24	11.41	4.14	0.81	99.59
II.	51.64	23.98	0.18	3.82	[5.01]		15.37	100.00
III.	45.44	32.88	trace	2.08	[4.63]		14.97	100.00
IV.	61.54	17.04	trace	4.92	1.75	2.03	13.70	100.98

The alteration of the orthoclase to zeolites has been effected by water charged with carbon dioxide. L. J. S.

**Formation of Pseudophite in Granitic Rocks.** By H. STADLINGER (*Zeit. Kryst. Min.*, 1901, 35, 313—315; from *Sitz.-Ber. phys.-med. Soc. Erlangen*, 1899, 31, 1—63).—Large porphyritic crystals of fresh

microcline, with some intergrown plagioclase, from the granite of Strehlerberg in the Fichtelgebirge, gave on analysis the results under I; sp. gr. 2·559. The following stages in its alteration are traced out, the end product being pseudomorphs of pseudophite, of which the composition is given under II; sp. gr. 2·6397. The microcline first loses its lustre and becomes coated with rusty-brown limonite; later, in the outer zone and along cleavage cracks, it becomes green; still later, the felspar is completely kaolinised, the colour passing to greyish-green, and finally to dark olive-green. Under the microscope, the following stages are recognised: complete kaolinisation of the enclosed laths of plagioclase; commencing turbidity of the microcline; formation of secondary quartz and muscovite; destruction of the 'cross-hatched' structure; development in the exterior portions of a green colour and of scales of lithia-iron-mica; accumulation of rutile needles; appearance of zircon; finally, the destruction of the grains of kaolin and the remains of the felspar.

The analysis of the "pseudophite" shows it to be a chloritic substance intermediate between pennine and clinocllore; its composition can be expressed as 62·71 amesite molecules and 47·29 antigorite molecules. A granular dolomite at the granite contact explains the large increase in the amount of magnesia:

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O. Loss on at 100° ignition.	Total.
I.	62·96	19·36	0·40	1·18	—	0·90	0·86	11·94	2·51	0·09	100·44
II.	30·30	20·06	1·63	5·30	—	0·87	28·28	1·32	1·40	0·74	101·79
III.	45·80	6·52	18·03	6·13	1·52	4·63	1·76	1·17	1·39	9·90	100·80

Analysis III is of nontronite, which occurs near Strehlerberg as an alteration product of a schistose amphibolite: the material analysed contained some undecomposed hornblende, as well as a little mica, magnetite, and quartz.

L. J. S.

[Analyses of Garnet and Gold.] By W. REISS and A. STÜBEL (*Zeit. Kryst. Min.*, 1901, 35, 298—301; from *Geologische Studien in der Republik Colombia. II. Petrographie, Berlin*, 1899).—The following mineral analyses are contained in an account of the minerals of Colombia. Rhombic dodecahedra of garnet of a greenish-grey colour, sometimes reddish in the interior, and optically anomalous, from La Topa, gave the following results. The magnesia probably belongs to enclosed malacolite.

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Loss on ignition.	Total.
40·03	21·14	2·37	34·46	2·03	0·53	100·56

Alluvial gold from various localities gave, on analysis by Kollbeck, the following results; small amounts of copper and iron are also present:

Au.	80·43	83·33	89·00	77·53	84·84	71·13	72·29	87·98	83·49
Ag.	17·89	13·56	9·43	20·89	13·63	24·09	24·42	11·03	14·79

L. J. S.

Theory of Tourmaline Mixtures. By GUSTAV TSCHERMAK (*Zeit. Kryst. Min.*, 1901, 35, 209—219. Compare *Abstr.*, 1900, ii, 217).—A reply to Penfield (*Abstr.*, 1900, ii, 602). The author upholds the

view that the composition of tourmalines can be better expressed by the isomorphous mixing of two definite compounds rather than by the substitution formula of Penfield.

L. J. S.

**A Stony Meteorite which fell at Felix, Alabama.** By GEORGE P. MERRILL (*Proc. U.S. Nat. Museum*, 1901, 24, 193—198).—This stone, weighing 2049 grams, was seen to fall on May 15th, 1900, near Felix in Perry County, Alabama. The broken surfaces are dark smoky grey, almost black in colour. The material is soft and friable and is very fine grained, with numerous small chondrules. Sp. gr. 3·78. The microscopic structure is described as follows: in a very dense, dark grey, seemingly amorphous base are scattered olivine, augite and enstatite in the form of fragments and chondrules, and interspersed with occasional minute blebs of native iron and troilite. From analyses by P. Fireman of the metallic portion and of the soluble and insoluble silicates, the composition of the stone is:

Fe.	Ni.	Co.	Cu.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Cr <sub>2</sub> O <sub>3</sub> .	FeO.	FeS.
2·59	0·36	0·08	0·01	33·57	3·24	0·80	26·22	4·76
MnO.	NiO,CoO.	CaO.	MgO.	K <sub>2</sub> O	Na <sub>2</sub> O.	C.	H <sub>2</sub> O.	Total.
0·68	1·01	5·45	19·74	0·14	0·62	0·36	0·16	99·79

The mineralogical composition is: metal 3·04, troilite 4·76, chromite 1·17, graphite 0·36, soluble silicate (olivine in part) 72·60, insoluble silicate (enstatite and augite in part) 18·07 = 100·00.

L. J. S.



## Physiological Chemistry.

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**Physical and Chemical Phenomena of Respiration at High Altitudes during a Balloon Ascent.** By J. TISSOT and HALLION (*Compt. rend.*, 1901, 133, 949—951).—At altitudes up to 3500 metres the proportion of oxygen absorbed and carbon dioxide exhaled increases with the altitude, so that the blood takes up practically the same quantity of oxygen per minute, whatever the altitude up to the limit stated. The volume of air inhaled, measured at the actual temperature and pressure, varies little, but tends to diminish at high altitudes. The variations in the respiratory quotient follow an order the inverse of that which would be followed if the exhaled carbon dioxide obeyed the laws of solutions of gases. C. H. B.

**Changes in the Hæmoglobin of Blood under low Atmospheric Pressure.** By J. VALLOT (*Compt. rend.*, 1901, 133, 947—949).—Experiments were made at different heights on Mont Blanc and in a balloon, the quantity and rate of reduction of the hæmoglobin being determined by means of Henocque's hæmatospectroscope. The results

show that a reduction in the pressure of the air at once produces an increase in the activity of the exchanges in human blood, and thereby compensates for the diminution in the mass of oxygen in a given volume of the air. The activity of the reduction is practically the inverse of its duration, since the actual quantity of hæmoglobin in the blood varies but little, even at high altitudes. Mountain sickness is due to an increase in the duration of reduction, and the fatigue of climbing tends to prevent the diminution in the duration of reduction and may produce the same change as accompanies mountain sickness. Rest at high altitudes promotes the re-establishment of the physiological functions. After descent, the return to normal conditions is slower the longer the sojourn at a high altitude and the more complete the acclimatisation to it.

C. H. B.

**Dissociation of Carboxyhæmoglobin.** By NESTOR GREHANT (*Compt. rend.*, 1901, 133, 951—952).—A dog was allowed to breathe first air containing 1 per cent. of carbon monoxide for 12 or 15 minutes and then air or oxygen, the quantity of carbon monoxide in the blood being determined from time to time. The following figures, representing the quantity of carbon monoxide in 100 c.c. of blood, show that the elimination is much more rapid with oxygen than with air:

Time after poisoning	0	10	20	30	40	50	mins.
Breathing air.....	14·7	14·6	14·5	12·8	11·4	10·2	c.c.
Breathing oxygen...	23·7	16·9	10·1	8·2	5·7	4·2	c.c.

C. H. B.

**Metabolism in Man.** By L. SPIEGEL (*Virchow's Archiv*, 1901, 166, 364—371).—The investigation relates to the metabolism of sulphur compounds. In the oxidative decomposition of proteids in the body, cystin and hyposulphurous acid are constantly formed. These are not final products but are further oxidised under normal circumstances. The appearance of cystin or hyposulphites in the urine points to diminution of oxidation. The condition is compared to what occurs in regard to sugar in diabetics.

W. D. H.

**The Passage of Proteid through the Intestinal Wall.** By OTTO COHNHEIM (*Zeit. physiol. Chem.*, 1901, 33, 451—465).—The disappearance of peptone when in contact with the intestinal wall, as described by Hofmeister, Neumeister and others, does not depend on its assimilation or regeneration into ordinary proteid, but on its further decomposition into simpler decomposition products. This is accomplished by a special ferment, *erepsin*, secreted by the intestinal mucous membrane. Erepsin has no action on ordinary proteid, but only on peptone, and on a part of the proteoses. Leucine and tyrosine were separated from the products; no tryptophan was found.

W. D. H.

**The Absorption of Substances insoluble in Water.** By HANS FRIEDENTHAL (*Pflüger's Archiv*, 1901, 87, 467—472).—Largely polemical, against Höber. In continuation of previous work, it is now shown that finely divided metallic mercury is absorbed; this is mainly attributed to leucocytic action.

W. D. H.

**Molecular Concentration of the Blood and Tissues of Aquatic Animals.** By LÉON FREDERICQ (*Bull. Acad. Roy. Belg.*, 1901, No. 8, 428—454).—In the lowest animals, the blood or hæmolymp has the same molecular concentration and the same percentage of salts as the water in which they live. In the next stage of evolution, the molecular concentration is the same, but the amount of salt is less than in the sea-water. Finally, as the surfaces of exchange become more highly developed and less permeable, both the molecular concentration and the amount of salt are very different in the two fluids. The same three stages are seen in the tissues. Numbers obtained with numerous animals are given which support these propositions. W. D. H.

**Hæmolysis and Bacteriolysis.** By W. BULLOCK (*Trans. Path. Soc.*, 1901, 52, 208—245).—As a result of the injection of ox-blood into rabbits, a hæmolysin develops in three days; it consists of two substances, an 'immune substance,' and a thermo-unstable complement. Experiments show it is possible to make quantitative estimations of these substances. The appearance of the immune substance is coincident with an increase of mono-nuclear leucocytes; it is probably formed in the lymphatic tissues, whilst the complement is probably formed in myeloid tissue. The immune substance is excreted in the milk; this partly explains the immunity of the offspring; the hæmolysin, however, reaches the fœtus mainly by the placenta. There is a close analogy between hæmolysis and bacteriolysis.

W. D. H.

**Natural Anti-hæmolysins.** By BESREDKA (*Ann. Inst. Pasteur*, 1901, 15, 785—807).—Both man and animals make normally for their own red corpuscles an anti-hæmolysin which is very probably an anti-auto-hæmolysin.

W. D. H.

**Influence of Salts on Heart Muscle.** By WILLIAM H. HOWELL (*Amer. J. Physiol.*, 1901, 6, 181—206).—The experiments were performed on the ventricular muscle of the terrapin's heart. Spontaneous contractions depend on the presence of both calcium and sodium compounds. Sodium salts tend to produce relaxation; calcium salts increase its tone, and this may pass into a condition of rigor. Potassium chloride antagonises this effect of calcium chloride, but only to a marked extent when sodium salts are present in approximately normal proportions. When all these salts are present, automatic contractibility is maintained longer. Strips of the ventricle do not contract spontaneously in the animal's own serum or an equivalent Ringer's mixture; this is due to the inhibitory influence of the potassium salts. When the heart is placed in a 0.7 per cent. solution of sodium chloride, the effects observed are first due to the gradual loss of potassium from the heart muscle by diffusion, and the final disappearance of the beats is due to a similar loss of calcium.

W. D. H.

**Copper in the Liver of Cephalopods.** By MARTIN HENZE (*Zeit. physiol. Chem.*, 1901, 33, 417—425).—The relationship of the liver of vertebrates to the iron of the blood suggested a similar investigation of the cephalopod liver in reference to copper. The

blood of these animals is free from iron. The blood-free liver contains a small amount of iron, but the amount of copper is about ten times as great. Both metals are united to nucleo-proteid. Dastre and Floresco (*Arch. de Physiol.*, 1898, 10, 289) describe two pigments in the liver of these animals, one is insoluble in water but soluble in chloroform; this xanthophylloid pigment is free from both metals; the other pigment, which is soluble in water, was prepared in an impure form and contains from 1.3 to 7.7 per cent. of copper, 0.7 per cent. of iron and 4.7 per cent. of phosphorus. W. D. H.

**Chemical Constituents of Tendon.** By LEO BUERGER and WILLIAM J. GIES (*Amer. J. Physiol.*, 1901, 6, 219—231).—The average composition of the tendon Achilles is thus given :

	Calf.	Ox.
Water .....	67.51	62.87
Solids .....	32.49	37.13
Inorganic matter.....	0.61	0.47
Organic matter .....	31.88	36.66
Fat .....	—	1.04
Albumin and globulin .....	—	0.22
Mucoid.....	—	1.28
Elastin.....	—	1.63
Collagen .....	—	31.58
Extractives (creatine, purine bases, &c.) .....	—	0.89

W. D. H.

**The Fat of the Egg of the Common Fowl.** By THOMAS E. THORPE (*Arch. Néer. sci. exact. nat.*, 1901, [ii], 6, 155—161).—Eggs from pure bred hens (Horsley) and from hens of mixed breeds (High Pitfold) gave ratio of yolk to white, 1:1.92 and 1:1.62 respectively. The percentage of fat in the yolk was 31.7 in the Horsley eggs and 30.6 in the High Pitfold eggs, corresponding with 9.4 per cent. of fat in the former eggs and 10.2 in the eggs from High Pitfold. The fat from the Horsley eggs contained 0.6 per cent. of phosphorus, corresponding with 15.04 per cent. of lecithin, 61.5 per cent. of neutral fat, and 23.2 per cent. of free acids. The neutral fat had a saponification value of 181.5 and contained 93.1 per cent. of insoluble and 2.04 per cent. of soluble (total 95.14 per cent.) acids. The saponification value of the insoluble acids was 189.6 (mol. wt. = 296). When calculated on the assumption that only triglycerides were present, there should be 95.93 per cent. of fatty acid (in agreement with 95.14 per cent. found) and 9.86 per cent. of glycerol, whilst if monoglycerides alone were present there should be only 87.79 per cent. of fatty acid and 29.58 per cent. of glycerol. Determination of the glycerol showed 9.6 per cent. (mean) in the fat. Results obtained with the High Pitfold eggs also show that only triglycerides are present in the fat. J. McC.

**Proteids of Cow's Milk.** By GUSTAV SIMON (*Zeit. physiol. Chem.*, 1901, 33, 466—541).—This paper is mainly concerned with quantitative methods. A large number of methods for the estimation of total proteids and of the individual proteids are carefully compared. Analyses of cow's milk and colostrum are given. W. D. H.

**Physiological Action of Decoction of Mussels.** By CONSTANT THIBERT (*Bull. Acad. Roy. Belg.*, 1901, No. 8, 494—499).—In decoction of mussels there exists a substance which on intravenous injection in the dog produces a lowering of arterial pressure, an increased production of lymph, and a non-coagulable condition of the blood. The action is similar to that produced by 'peptone.' The active substance was not isolated. Glycogen takes no part in the effects. W. D. H.

**The Action of Pilocarpine and Atropine on Echinoderm Embryos.** By ALBERT P. MATHEWS (*Amer. J. Physiol.*, 1901, 6, 207—215).—Atropine sulphate, in small doses, hinders the development and gives rise to dwarf embryos. Pilocarpine hydrochloride hastens development and gives rise to abnormally large embryos. The action of atropine resembles that of hydrogen ions, the action of pilocarpine that of hydroxyl ions. Hence atropine and pilocarpine act on animal cells directly, and not merely on secretory nerve-endings. It is suggested that atropine inhibits, and pilocarpine increases, oxidation processes, and that this will explain their action on secretory cells.

W. D. H.

**Pathogenic Properties of Trypsin and the Antitryptic Power of Guinea-pig's Serum.** By PIERRE ACHALME (*Ann. Inst. Pasteur*, 1901, 15, 737—752).—The introduction into animals, subcutaneously or intraperitoneally, of trypsin, a substance capable of profoundly altering 'living proteid,' provokes immediately a process of defence. This consists of an exudation of blood-serum (? plasma or lymph) under the influence of vaso-motor nerves. The exudation opposes the penetration of the trypsin and then neutralises its effects. When this is frequently repeated, the process of defence is more perfect and this is due to an increase in the antitryptic power of the serum. W. D. H.

**Intravenous Inoculation of a Diplococcus isolated from Cases of Rheumatic Fever.** By F. J. POYNTON and ALEXANDER PAINE (*Trans. Path. Soc.*, 1901, 52, 248—253).—Rheumatism appears to be due to a diplococcus which can be separated from heart, lungs, joints, &c., of rheumatic fever patients. When it is intravenously injected into rabbits, arthritis is the usual result.

W. D. H.

**Analysis of the Urine in a Case of Osteomalacia.** By THOMAS (*J. Pharm. Chim.*, 1901, [vi], 14, 437—438).—The paper contains complete analyses of the urine both before and after administration of calcium glycerophosphate. The effect of the calcium glycerophosphate is to render the urine much more normal in composition. H. R. LE S.

**Concretions from the Urinary Duct of a Wild Boar and from the Kidney of a Deer.** By CONSTANTIN COUNCLER (*Chem. Zeit.*, 1901, 25, 872—873).—A concretion from the urinary duct of a wild boar (*Sus scrofa*) consisted almost entirely of pure crystallised magnesium ammonium phosphate. A second concretion from the kidney of a deer (*Cervus capreolus*) consisted of pure crystallised calcium oxalate,  $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$

J. J. S

## Chemistry of Vegetable Physiology and Agriculture.

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**The Effect of Nitrates on certain Bacteria.** By WALTER C. C. PAKES (*Trans. Path. Soc.*, 1901, 52, 246—247).—The effect of high percentages of nitrates on the morphology of certain bacteria is described. The bacilli resume their original form when again planted on broth. W. D. H.

**The Lactic Ferments in the Arts.** By MARTINUS W. BEYERINCK (*Arch. Néer. sci. exact. nat.*, 1901, [ii], 6, 212—243).—The ferments used in producing lactic acid have been exhaustively studied. The bacteria are *Lactococci* and *Lactobacilli*. Lactic fermentation is not a mere enzymic action, but is a true catabolic process. Experiments with pure cultures of lactic ferment prove that the quantity of acid formed is dependent on the temperature (optimum 41°) and on the presence or absence of air. The author applies the name *Lactobacillus delbrücki* to all those species which can be isolated from the ferment by the gelatinised must method; *L. delbrücki* is not the active agent of a good industrial ferment. *Lactobacillus fermentum* has also been isolated from the ferment and it is shown that this is the bacterium which gives the ferment its particular character. Cultivated under good aëration, it gives only lactic acid and no volatile acids; its optimum is 41—42°, its minimum 25°, and its maximum 50°.

*L. fermentum* can be transformed into *L. delbrücki* by cultivation above the optimum temperature and by prolonged cultivation under very profuse aëration; the reverse transformation can be carried out by an aerobic culture at the ordinary temperature. J. McC.

**Decomposition of Butter Fat by Micro-organisms.** By O. LAXA (*Arch. Hygiene*, 1901, 41, 119—151).—The most active agents in the decomposition of butter fat among those examined were the moulds, *Oidium lactis*, *Penicillium glaucum*, and a species of *Mucor*, as well as *Bacillus fluorescens liquefaciens*. Several varieties of yeast and of bacteria which are able to peptonise casein were found to have only a slight action, whilst a number of varieties of lactic acid bacteria and of *Tyrophrix* were found to be inactive. The decomposition of the fat is not due to the action of ammonia produced from the nitrogenous matter by the action of the organisms, as has been suggested by Duclaux, since solutions of ammonia do not act on the fatty glycerides at the ordinary temperature. In the cases of *Penicillium* and *Mucor*, it was found possible, by grinding the mould with glass powder and filtering, to obtain a sterile solution containing an enzyme which decomposed monobutyryl and butter fat in the characteristic manner. Of the glycerides of the insoluble acids, those of highest molecular weight are first decomposed. On the other hand, the glycerides of the soluble acids of lowest molecular weight are most largely decomposed. This appears to be connected with the fact that the higher soluble acids exert a very strong deterrent effect on the growth of the organisms. The free volatile fatty acids are then further decomposed by the action of the mould. Experiments with casein freed from fat show that no

part of the fatty acid produced is derived from the casein, but that the organism is able to synthesise a small amount of fat which is stored in its cells as reserve material. A. H.

**Formation of Volatile Acids in Alcoholic Fermentation.** By W. SEIFERT (*Bied. Centr.*, 1901, 30, 774—776; from *Zeit. landw. Versuchs-Wes. Oesterr.*, 1901, 4, 227).—Volatile acids were not produced in any quantity (0.6 gram per litre being the largest amount) in must by Tokay yeast. When greater amounts occur in wines, their presence must be attributed to moulds or acetic acid bacteria. Differences in temperature had very little effect on the formation of volatile acids, but rather more was produced at 15° than at 30°. The presence of tartaric or malic acid had no appreciable effect. The amount of non-volatile acid was distinctly increased during fermentation; addition of tartaric or malic acid to the must somewhat diminished the production of non-volatile acid. N. H. J. M.

**Production of Hydrogen Sulphide in Alcoholic Fermentation.** By W. SEIFERT (*Bied. Centr.*, 1901, 30, 776—778; from *Zeit. landw. Versuchs-Wes. Oesterr.*, 1901, 4, 221).—The results of fermentation experiments with 0.2 gram of sulphur in 250 c.c. of must showed that the greatest production of hydrogen sulphide took place after the vigour of the fermentation had begun to diminish. The amount of sulphide produced in two weeks was 0.0073 gram per litre.

It was found that the presence of sulphur in the amount employed quickened the fermentation as compared with fermentation in absence of sulphur. This is shown to be probably partly due to mechanical action, wood and paper fibre having a similar effect. In practice, the amount of sulphur would be considerably less than 0.8 gram per litre and insufficient to exercise either a mechanical or an antiseptic action.

In the aeration of must, the stirring and distribution of the yeast is probably of greater importance than the access of air. N. H. J. M.

**Fluorine in Musts and Wines.** By KARL WINDISCH (*Zeit. Nahr. Genussm.*, 1901, 4, 361—368).—See this vol., ii, 104.

**Chemical Processes in the Killed Yeast Cell.** By ROBERT ALBERT and W. ALBERT (*Centr. Bakt. Par.*, 1901, ii, 7, 737—742).—When yeast which has been killed by treatment with alcohol and ether is suspended in water, coagulable albumin and non-coagulable proteids pass out of the cell and are rapidly digested by the proteolytic enzyme of the yeast, which does not appear to be affected by the treatment with alcohol. The liquid filtered after 48 hours still contains this proteolytic enzyme together with the products of its action. Microscopic examination shows that this change is accompanied by the disappearance of material from the cell, deeply staining granules being left, which afterwards also disappear, leaving a small mass, capable of being stained, which is possibly the nucleus of the cell. The zymase of the cell, although still active and capable of bringing about the fermentation of the glycogen within the cell or of sugar solution, does not pass out of the cell. It seems probable also that the glycogen is first hydrolysed by another ferment, which, like the zymase, remains in the cell, since glycogen added to the solution is neither hydrolysed

nor fermented. The zymase itself is destroyed in about 20 hours by the proteolytic enzyme. Invertase also passes out of the cells so rapidly when they are placed in water that a solution of considerable inverting power is formed which only contains traces of albumins; attempts are being made to prepare pure invertase by this means.

A. H.

**Respiration of Hydrogen and Hydrocarbons through the Green Parts of Plants.** By GINO POLLACCI (*Chem. Centr.*, 1901, ii, 938—939; from *Atti R. Ist. Bot. Univ. Pavia*).—The production of formaldehyde in the green parts of plants is attributed to the action of nascent hydrogen. Both hydrogen and hydrocarbons were found to be given off by plants.

N. H. J. M.

**Nutrition of Plants at the Expense of the Cotyledons.** By GUSTAVE ANDRÉ (*Compt. rend.*, 1901, 133, 1011—1013).—The amounts of dry matter, ash, silica, calcium, phosphoric acid, potassium, and nitrogen were determined in Spanish haricots and in the cotyledons and plants at intervals of two days, commencing nine days after sowing the seeds. The results are arranged to show the gradual exhaustion of the cotyledons and the coincident increase in the plants of the various constituents.

Silica and calcium are absorbed from the commencement, being, as previously shown, withdrawn from the soil by the cotyledons. Nitrogen and phosphoric acid remain unchanged for some time, the grain in the plant being accounted for by corresponding losses in the cotyledons. The assimilation of phosphoric acid from the soil commences at the same time as the assimilation of soil-nitrogen. The absorption of potassium from the soil commences as soon as the germinating period ends.

N. H. J. M.

**Chlorophyllous Assimilation in the Autumn.** By JEAN FRIEDEL (*Compt. rend.*, 1901, 133, 840—841).—On repeating his experiments with glycerol extracts of leaves (*Abstr.*, 1901, ii, 411) in October and November, the author obtained negative results. It was, however, found that, at this time of the year, assimilation is very feeble in the leaves themselves. Further experiments will be made in the spring.

N. H. J. M.

**Mechanism of Esterification in Plants.** By EUGÈNE CHARABOT and A. HÉBERT (*Bull. Soc. Chim.*, 1901, [iii], 25, 955—959. Compare *Abstr.*, 1901, ii, 619).—Rhodinol is esterified more readily than geraniol; under comparable conditions, 83 per cent. of the rhodinol, and 67 per cent. of the geraniol are converted into the acetate. In a sample of Algerian geranium-oil, it was found that the esters contained a larger proportion of rhodinol than the free alcohols, showing that esterification in the plant obeys the usual laws, and that the esterified alcohols found in the plant are those which are most readily esterified under laboratory conditions.

T. M. L.

**Composition of the Reserve Carbohydrates of the Proteid of the Seeds of some Liliaceæ, and in particular of Butcher's Broom.** By GEORGES DUBAT (*Compt. rend.*, 1901, 133, 942—944).—Air-dried seeds of *Ruscus aculeatus* (with 9.88 per cent. of water)



yielded 0.97 per cent. of fatty matters and when digested for half-an-hour with 0.3 per cent. sulphuric acid on a water-bath, 13.616 per cent. of reducing sugar, calculated as invert sugar. A certain amount of lævulose was separated as calcium lævulosate.

When hydrolysed, the seeds yielded 69.85 per cent. of reducing sugars: mannose, 27.92; dextrose (?), 27.64; invert sugar, 13.61, and pentoses, 0.68 per cent. N. H. J. M.

**Origin of Starch in Wheat Grain.** By PIERRE P. DEHERAIN and C. DUPONT (*Compt. rend.*, 1901, 133, 774—778).—Whilst the total nitrogen of a wheat crop does not increase after the commencement of maturation (Isidore Pierre, *Recherches expér. sur la développement du blé*, 1866; Dehérain and Meyers, *Abstr.*, 1883, 493; and Berthelot, *Chim. Veg. Agric.*, 2, 259), there is a migration of nitrogen from the lower to the upper leaves, followed by a concentration in the grain.

In the case of starch, there is at no period a reserve of amylaceous matter, such as occurs in potatoes, tobacco, &c. The rapid accumulation of starch during the last weeks is therefore due to the elaboration of new substance, notwithstanding that the green portions of the plants are by this time very restricted. It is now shown that the green upper portions of the stems have the functions of leaves in decomposing carbon dioxide. It is further shown that whilst nitrogen and reducing sugars remain in the upper parts of the stems, the starch, dextrin, and non-reducing sugars migrate for the most part to the ears, where they are concentrated as starch.

The late production of starch, and its dependence on the stems remaining green, is illustrated by the results of field experiments in 1888 and 1889, when the weather was wet and dry respectively during the period of maturation. In 1888, the weight of grain was 3445 kilos., and contained 439 kilos. of nitrogenous matter, and 2689 kilos. of starch; in 1889, the yield of grain was 2922 kilos., and it contained 447 kilos. of nitrogenous matter and 1808 kilos. of starch per hectare.

N. H. J. M.

**Prussic Acid in Sweet Cassava.** By PATRICK CARMODY (*Lancet*, 1900, Reprint).—The presence of hydrocyanic acid in sweet cassava, first pointed out by Francis (*Abstr.*, 1877, ii, 515), is confirmed. It is further shown that the acid is located chiefly in the skin and outer cortical layer, whereas in the bitter cassava it is uniformly distributed throughout the tuber.

E. G.

**Chemistry of Stylophorum Diphylum.** By JULIUS O. SCHLOTTERBECK and H. C. WATKINS (*Pharm. Review*, 1901, 19, 453—458).—*Stylophorum diphylum*, commonly known in America as the yellow or celandine poppy, belongs to the *Papaveraceæ* and grows in the low woods from Ohio to Tennessee and westward to Wisconsin and Missouri. The following alkaloids were found to be present in the plant as salts of chelidonic acid: (1) chelidonine, for which the formula proposed by Schmidt and Selle is confirmed by analyses of the alkaloid and its salts; it is a tertiary base and contains no methoxy-groups. (2) A new alkaloid, *stylopine*,  $C_{19}H_{19}O_5N$ , of which the chloride, nitrate, hydriodide, aurichloride, and platinichloride have

been analysed; it does not contain methoxy-groups and is probably a tertiary base; (3) protopine; (4) a new alkaloid, *diphylline* which melts at  $216^{\circ}$ ; (5) sanguarine, identical with that found in *Sanguinaria*, *Chelidonium*, and *Bocconia*. Potassium chelidonate is present in the plant in considerable quantity. Besides the above substances, the plant also contains a crystalline colouring matter probably identical with chelidoxanthin, and a fragrant substance resembling coumarin in odour.

H. R. LE S.

**Does Argemone Mexicana contain Morphine?** By JULIUS O. SCHLOTTERBECK (*Pharm. Review*, 1901, 19, 458—461).—Mexican or prickly poppy (*Argemone mexicana*) does not contain morphine; the only alkaloids present are berberine and protopine. The alkaloid isolated from this plant by Peckolt, to which he gave the name argemonine, is probably identical with protopine.

H. R. LE S.

**Chemical Composition of the Roots of *Dorstenia Klaineana* (Gabon Ivy) and *D. Brasiliensis*.** By EDOUARD HECKEL and FREDERIC SCHLAGDENHAUFFEN (*Compt. rend.*, 1901, 133, 940—942).—The root of *Dorstenia Klaineana*, a shrub common in the French possessions in Africa, has a brick-red bark and a strong odour of coumarin. It contains *ψ-coumarin*,  $C_{12}H_5O_3$ , which melts at  $180^{\circ}$  and is soluble in light petroleum; various red resins, characterised by giving an intense cochineal coloration in contact with bromine vapour; tannin, and a large quantity of starch.

The root of *D. Brasiliensis* yields to light petroleum a crystalline substance which melts at  $189^{\circ}$  and gives a golden-yellow colour with strong sulphuric acid, a deep brown colour with a mixture of sulphuric and selenious acids; a golden-yellow colour, becoming violet and then blue, with sulphuric and iodic acids, and a violet tint changing to blue with sulphuric acid and potassium dichromate. The root also contains resins which seem to be identical with those from *D. Klaineana*. Both roots contain a very large proportion of inorganic matter, the ash consisting of calcium and ferric oxides, the latter in large quantity, as also are the sulphates, no chlorides, but a small quantity of phosphates.

C. H. B.

**Feeding Experiments, with Milch-sheep and Goats, on the Effect of Fat on the Amount and Composition of the Milk.** By C. BEGER, P. DOLL, G. FINGERLING, E. HANCKE, H. SIEGLIN, W. ZIELSTORFF and AUGUST MORGEN (*Chem. Zeit.*, 1901, 25, 951—953).—Fat, when fed in the form of sesamé cake or earth-nut oil, has, under certain conditions, a considerable effect on the amount of fat in the milk, and it is probable that these fats serve, at any rate to some extent, as materials for the production of milk-fat.

When the fat of a ration having a nutritive ratio of 1:3.6—3.7, and containing 1 gram of fat per kilo. of live weight, is replaced to the extent of four-fifths by an equivalent amount of carbohydrates, the milk-fat produced was reduced by about 14 grams per day, or about 34 per cent. of the normal amount.

Whilst a reduction in the amount of food-fat diminished the fat in

the dry matter of the milk by 7.1 per cent., there was invariably an increase in the amounts of sugar, nitrogen, and ash. An increased amount of food-fat up to a certain point increased the amount of milk-fat but not the other constituents.

The effect of food-fat in increasing the milk-fat is limited, and an excess of fat produces different effects with different animals.

N. H. J. M.

**Composition of Hard Wheat and the Physical Constitution of its Gluten.** By ÉMILE FLEURENT (*Compt. rend.*, 1901, 133, 944—947).—Analyses are given of Russian and African wheat grain and of Canadian goose wheat. Hard wheat contains above 2.5 per cent. of proteids more than soft wheat, and more gluten than the most highly nitrogenous soft wheats. The sum of the gluten and starch in wheat is a constant amount (65 per cent.), and the sum of the sugars and the soluble nitrogenous matters is also constant (5 per cent.). The results of determinations of gliadin in the flour of hard wheat by means of the two methods described by the author (*Compt. rend.*, 132, 1421, and 133, 327 and 754) are not concordant, owing to hard wheat containing 1.5 to 2 per cent. more soluble matter than soft wheat; even when the densimeter results are subjected to a correction, the results are much too low. This is due to the presence in the gluten of hard wheat of a considerable amount of conglutin. The gluten of flour from Russian wheat, for instance, contained gliadin 46.45, glutenin 37.89, and conglutin 15.66 per cent.

N. H. J. M.

**Composition of the Products Resulting from the Grinding of Wheat by means of Millstones and Rollers.** By LÉON LINDET (*J. Pharm. Chim.*, 1901, [iv], 14, 433—437).—The superiority of roller milling over the ordinary grinding by millstones is clearly seen from the analyses of the different constituent parts into which the wheat is separated by the two processes.

H. R. LE S.

**Influence of Single Manures on Barley.** By J. J. VANHA (*Bied. Centr.*, 1901, 30, 745—750; from *Zeit. landw. Versuchs-Wes. Oesterr.*, 1901, 4, 40).—Nitrogenous manure increases the yield of grain and straw much more than other manures, and, like potash, promotes root-growth. With increased root-production, there is also an increase in the number and weight of stems. The weight of single stems is, however, only increased by a mixture containing nitrogen, potassium, and phosphorus in moderate quantities. The length of the stems is increased by phosphates or potassium manure (up to 100 kilos. per hectare) and diminished by much nitrogenous manure. The number of ears is influenced much more by nitrogen than by phosphoric acid and potassium; the latter are without advantage in quantities greater than 100 kilos. per hectare. Nitrogenous manures, and in a much less degree, potassium and phosphoric acid, increase the number of grains by increasing the number of ears. All these manures, but especially nitrogen, increase the weight of grain; potassium seems to influence the volume of the grain the most. Phosphoric acid increases, whilst large amounts of nitrogen and potassium diminish, the mealiness of the

grain. The amounts of total nitrogen and of proteids are considerably reduced by phosphoric acid and potassium. Potassium is deposited to a greater extent in the straw than in the grain, whilst phosphoric acid is deposited chiefly in the grain. N. H. J. M.

**Experiments with Varieties of Barley.** By JOSEPH HANAMANN (*Chem. Centr.*, 1901, ii, 1126—1127; from *Zeit. landw. Versuchs-Wes. Oesterr.*, 4, 993—1006).—The results of experiments with old Bohemian and different Scotch varieties of barley showed that the heaviest and best variety (goldfoil) deteriorated most, notwithstanding the favourable climatic conditions. The other acclimatised varieties remained unaltered. The local conditions greatly affected the percentage of nitrogen.

The application of kainite resulted in a satisfactory gain in yield, whilst the amount of proteids was reduced.

The average percentage of nitrogen in a large number of samples of barley grown during ten years was 1.44. N. H. J. M.

**Influence of Manuring on the Composition of Potatoes.** By WALTER F. SUTHERST (*Chem. News*, 1901, 84, 258—259).—Analyses were made of potatoes grown (1) without manure, (2) with 20 tons of farmyard manure, and (3) 5 cwt. of superphosphate, 2 cwt. of potassium chloride, and 2 cwt. of ammonium sulphate per acre. The following percentage results were obtained :

	Dry Matter.	N.	Starch.	Ash.	K <sub>2</sub> O.	CaO.	P <sub>2</sub> O <sub>5</sub> .
1.	23.76	0.506	17.76	0.967	0.628	0.025	0.124
2.	21.92	0.516	13.56	0.973	0.635	0.022	0.147
3.	24.05	0.493	17.14	0.964	0.630	0.028	0.121

The similarity in the composition of the tubers from plots 1 and 3 is attributed to the absence of sufficient moisture in the soil to dissolve the artificial manures.

The starch was determined gravimetrically with Fehling's solution, after heating 3 grams of the dried substance successively with water at 108° and with dilute hydrochloric acid. N. H. J. M.

**Value of the Nitrogen in Pyrenean Phosphates.** By JULES JOFFRE (*Bull. Soc. Chim.*, 1901, [iii], 25, 960—961).—The small amount (0.14 per cent.) of nitrogen in phosphates from the Pyrenees was found to be of no agricultural value. T. M. L.

**Mixtures of Martin-slag and Degelatinised Bone-meal as Diluents for Basic Slag.** By FRANZ W. DAFERT and F. PILZ (*Chem. Centr.*, 1901, ii, 895; from *Zeit. landw. Versuchs-Wes. Oesterr.*, 4, 960—963).—An alleged sample of basic slag was separated by means of bromoform into a light portion (57 per cent.) consisting of degelatinised bone meal, and a heavy portion (40 per cent.), found to be martin-slag. The phosphate contained total P<sub>2</sub>O<sub>5</sub>, 16.63 per cent. and 14.3 per cent. soluble in citric acid solution. N. H. J. M.

## Analytical Chemistry.

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**Simple Gasometric Method of Estimating Chlorine, Hydrochloric Acid, Silver, and Phosphates.** By E. RIEGLER (*Zeit. anal. Chem.*, 1901, 40, 633—638).—Silver chloride, treated with hydrazine sulphate and sodium hydroxide, is decomposed according to the equation  $4\text{AgCl} + \text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4 + 6\text{NaOH} = 4\text{Ag} + 4\text{NaCl} + \text{Na}_2\text{SO}_4 + 6\text{H}_2\text{O} + \text{N}_2$ . By calculation 1 part of nitrogen corresponds with 20.424 parts of silver chloride: experiment gives 20.2 parts. The silver chloride (not more than a gram), precipitated and washed in the usual manner, is placed, together with about 0.5 gram of hydrazine sulphate, in the reaction flask of a Knop-Wagner azotometer, the inner vessel of which is charged with 10 c.c. of a 10 per cent. sodium hydroxide solution. After the temperature has been adjusted, as usual, the contents of the flask are shaken for 15 minutes, the temperature readjusted, and the volume of gas read off.

For the estimation of phosphoric acid, a quantity of a phosphate containing not more than 0.16 gram of  $\text{P}_2\text{O}_5$  is dissolved in dilute nitric acid, treated with 1—2 grams of silver nitrate and then with sufficient sodium hydroxide to produce a permanent precipitate, the precipitation of brown silver oxide being avoided. Dilute ammonia is then added until the liquid is alkaline to litmus paper, and the mixture boiled for 5 minutes. The silver phosphate is collected and washed, then dissolved in nitric acid. The silver is precipitated as chloride and estimated as above. One milligram of nitrogen is obtained for each 3.33 mg. of  $\text{P}_2\text{O}_5$ . M. J. S.

**Fluorine in Musts and Wines.** By KARL WINDISCH (*Zeit. Nahr.-Genussm.*, 1901, 4, 961—968).—Mention is made of several instances where the must from Spanish grapes could not be induced to ferment, owing, as it appeared afterwards, to the presence of a fluoride. The various methods for the qualitative detection of fluorine are reviewed, and preference is given to the test by etching glass.

An accurate estimation of fluorine in foods is still a *desideratum*. The great difficulty seems to be the prevention of loss of fluorine by volatilisation when reducing the substance to ash. L. DE K.

**Estimation of Sulphur in Iron Pyrites.** By R. AUZENAT (*Chem. Centr.*, 1901, ii, 1093; from *Mon. sci.* 1901, [iv], 15, 11, 635).—0.5 gram of the sample is oxidised with nitrohydrochloric acid with addition of 20 c.c. of a 10 per cent. solution of sodium chloride. The excess of acid may then be evaporated at  $120^\circ$  without any fear of losing sulphuric acid. At least six hours should elapse before collecting the barium sulphate. L. DE K.

[Discrimination between and Estimation of Pyrites and Marcasite in Mixtures.] By HENRY N. STOKES (*Bull. U.S. Geol. Survey*, 1901, No. 186, Ser. E., *Chem. and Physics*, No. 35).—See this vol., ii, 87.

**Estimation of Persulphates.** By CHARLES A. PETERS and SETH E. MOODY (*Amer. J. Sci.*, 1901, [iv], 12, 367—376).—The authors have investigated the various processes in use for the estimation of persulphates. The process introduced by Leblanc and Eckardt (reduction with ferrous sulphate and titration of the excess with permanganate) is simple, rapid, and convenient. Grützner's method (reduction at the boiling point with arsenious acid in alkaline solution and titration of the excess with iodine) is not trustworthy without a correction. Mondolfo's process (heating with potassium iodide and titrating the liberated iodine with thiosulphate) is simple and fairly rapid, but tends to give too low results. The method recently proposed by Namias where the potassium iodide is allowed to act for twelve hours in the cold also gives low results.

Gooch and Smith's process for the estimation of chlorates (*Abstr.*, 1892, ii, 236) by means of arsenic acid and potassium iodide may also be applied to persulphates; the results are accurate, but the process is less simple than the other methods.

L. DE K.

**Estimation of Alkali Persulphates.** By G. ALLARD (*J. Pharm. Chim.*, 1901, [vi], 14, 506—508).—The method usually employed for the estimation of alkali persulphates, which consists in the estimation of the iodine liberated when a solution of potassium iodide is added to the persulphate solution, is accurate only when carried out in neutral solution. If carried out in sulphuric acid solution, as recommended by Moreau (*Bull. Soc. Pharm.*, 1901, 3, 179), the results are too high, due to the fact that the sulphuric acid liberates iodine from the potassium iodide.

H. R. LE S.

**Rôle of Phosphoric Acid in Wine Analysis.** By RUDOLF WOX (*Zeit. öffentl. Chem.*, 1901, 21, 415—420).—Phosphoric acid, although no longer regarded as of much importance in judging the purity of a wine, is to be considered as a disturbing factor in estimating the other constituents of wine ash. The author has already explained that part of the acid may be converted into pyrophosphoric acid and so escape precipitation with molybdate solution (*Abstr.*, 1901, ii, 344). It is now shown that the potassium carbonate of the wine ash acts to some extent on the calcium phosphate with formation of calcium carbonate and potassium phosphate. The estimation of the alkalinity, according to the German official process, becomes, therefore, slightly incorrect in the presence of much phosphoric acid. The matter requires further investigation.

L. DE K.

**Methods for the Analysis of Artificial Manures.** By F. KRETSCHMER (*Zeit. angew. Chem.*, 1901, 14, 1136—1138).—Conventional methods are given for the partial or full analysis of phosphatic and nitrogenous artificial manures.

L. DE K.

**Analysis of Mixtures of Alkali Silicates, Carbonates, Sulphates and Hydroxides.** By GEORG LUNGE and W. LOHÖFER (*Zeit. angew. Chem.*, 1901, 14, 1125—1134).—The idea that sodium silicate is completely decomposed by barium chloride is incorrect; about 40

per cent. remains in solution and apparently increases the free alkalinity. The presence of silicic acid introduces an error when phenolphthalein is used as indicator on account of its acidic properties; the silica is, however, rendered inert if the liquid contains sufficient sodium chloride. Solutions containing carbonate may be fairly accurately titrated with phenolphthalein as indicator, provided they are sufficiently diluted and contain sodium chloride, or, what amounts to the same thing, a fair proportion of sodium hydroxide; the concentration of the alkali should not exceed one gram-mol. of sodium chloride per litre. For the estimation of the total alkali, the best process is titration with hydrochloric acid in the presence of methyl-orange. The following scheme is given for the technical analysis of the soda cake used in the manufacture of fibre: 1. *Insoluble matter* is estimated as usual. 2. *Alkalinity*. Twenty c.c. of the solution (50 grams dissolved to 500 c.c.) are titrated with *N*-hydrochloric acid and phenolphthalein until colourless and the titration is then continued with methyl-orange as indicator. 3. *Sodium sulphide and sulphite*. Twenty c.c. are diluted to 200 c.c., acidified with acetic acid, and rapidly titrated with *N*/10 iodine. 4. *Sodium sulphite only*. One hundred c.c. are precipitated with an alkaline solution of zinc acetate, the whole is diluted to 250 c.c., and filtered; 50 c.c. of the filtrate are then again acidified with acetic acid and titrated with iodine. 5. *Sodium silicate*. Twenty c.c. are evaporated with addition of hydrochloric acid and the silica separated as usual. 6. *Sodium sulphate*. The filtrate from the silica is precipitated with barium chloride as usual. The usual calculation is then applied.

L. DE K.

**Modification of Schumann's Apparatus for Estimating the Specific Gravity of Cement.** By P. BECK (*Zeit. anal. Chem.*, 1901, 40, 646—649).—Instead of oil of turpentine, carbon tetrachloride is employed; its lower viscosity shortens the operation materially. The adjustment of the liquid to the zero of the graduation is facilitated by having a hole in the side of the neck, and another in the graduated tube, which can be brought into communication by rotating the tube in the neck. Several additional devices enable a series of estimations to be performed rapidly.

M. J. S.

**Examination of Mixtures of Portland Cement and Slag Meal.** By P. BECK (*Zeit. anal. Chem.*, 1901, 40, 649—666).—Recent experiments by W. Fresenius show that a high consumption of permanganate (see Abstr., 1884, 876) can no longer be regarded as a criterion of the adulteration of Portland cement with slag meal. Attention has therefore been directed to the estimation of the sulphur existing as sulphide, this being the most characteristic constituent of slag when compared with genuine cement. Three methods were employed: (1) The total sulphur was estimated by fusing the substance with alkali carbonates and nitrate and heating the solution with nitric acid; the sulphur present as sulphate was also estimated after boiling the substance with hydrochloric acid. The difference was assumed to represent the sulphur of the sulphides. (2) The substance was decomposed by boiling with hydrochloric acid in a current of carbon dioxide

and the hydrogen sulphide absorbed by cadmium chloride, as in Fresenius' method of estimating sulphur in cast iron. (3) The consumption of permanganate by the substance was ascertained, and also the amount of permanganate required after the substance had been digested in the cold with dilute sulphuric acid and a cadmium salt. The difference, calculated according to the equation  $6\text{KMnO}_4 + 5\text{S} = 3\text{K}_2\text{O} + 6\text{MnO} + 5\text{SO}_3$ , agreed closely with the amount of sulphide-sulphur estimated according to method (1) in the slag-meal itself, and with the calculated amount in mixtures of the slag-meal with a sample of Portland cement which did not contain sulphides. This method is the most rapid of the three. It is carried out exactly as follows: The weighed substance (1 gram) is made into a paste with 50 c.c. of water in a flask, 100 c.c. more water are added and an excess of permanganate solution (5 grams per litre) with vigorous shaking, then immediately 50 c.c. of dilute sulphuric acid in small portions. By adding the reagents in this order, all loss of hydrogen sulphide is prevented. An excess of titrated ferrous ammonium sulphate solution is then added and the excess titrated back with the permanganate. A similar experiment is then made, in which 1–2 grams of cadmium carbonate are added to the wetted cement instead of the permanganate. Sulphuric acid is added as before and the flask is filled with carbon dioxide and corked. When the mixture has become clear, it is filtered and the filtrate immediately titrated with a permanganate solution one-fifth the strength of the former one.

M. J. S.

**Volumetric Estimation of Manganese.** By FRED IBBOTSON and HARRY BREARLEY (*Chem. News*, 1901, **84**, 247–248).—In the bismuthate process, 1.1 grams of the metal are dissolved in 35 c.c. of nitric acid of sp. gr. 1.20, and bismuthate added to the cooled solution until a permanganate colour persists or manganic oxide separates on boiling. The solution is cleared with hydrogen peroxide, sulphurous acid or ferrous sulphate, cooled, treated with 10 c.c. of water and excess of bismuthate, filtered, washed with 3 or 4 per cent. nitric acid, mixed with excess of ferrous ammonium sulphate, and titrated with decinormal permanganate. With hydrogen peroxide, the results are liable to be too high. The presence of chromium only affects the results in warm solutions or when contact with the bismuthate is prolonged. Tungsten does not affect the reaction, but any hydrofluoric acid must be eliminated. Titanium and vanadium may prove troublesome and molybdenum is so when hydrogen peroxide is used, but not with ferrous sulphate (compare Ramage, this vol., ii, 50).

D. A. L.

**Volumetric Estimation of Manganese.** By LAWRENCE DUFTY (*Chem. News*, 1901, **84**, 248).—0.1 gram of steel is dissolved in 2 or 3 c.c. of nitric acid according to the amount of carbon present, the carbon estimated, the solution diluted with nitric acid in a test-mixer to 20 c.c., when the manganese is under 0.8 per cent. or otherwise to 25 c.c., and then mixed with 0.2 gram of bismuthate. After settling, 5 c.c. of the clear solution are compared colorimetrically with a standard. The process is a modification of that of Reddrop and Ramage (*Trans.*, 1895, **67**, 268).

D. A. L.



**Volumetric Estimation of Manganese.** By HUGH RAMAGE (*Chem. News*, 1901, **84**, 269. Compare preceding abstracts).—The author defends his statements against criticisms of Ibbotson and Brearley, and expresses disapproval of the use of ferrous sulphate or ammonium ferrous sulphate as a substitute for hydrogen peroxide in the manner suggested by those authors. Moreover, he prefers titration to the colorimetric method of Dufty. D. A. L.

**New Process for the Estimation of Manganese.** By GEORG VON KNORRE (*Zeit. angew. Chem.*, 1901, **14**, 1149—1162).—Marshall (*Trans.*, 1891, **59**, 771—786) has stated that manganous salts when mixed with potassium persulphate yield manganese dioxide. The author has succeeded in making this the basis of a quantitative estimation. Solutions of manganous salts, which must first be converted into sulphate, on boiling with excess of ammonium persulphate yield the whole of the metal as dioxide, which may then be collected and treated either gravimetrically or volumetrically. In the presence, however, of copper, nickel, zinc, iron, or cobalt, the dioxide carries down a portion of these metals; in the absence of cobalt, good results may even then be obtained by applying the volumetric process with standard hydrogen peroxide (or ferrous sulphate) and standard potassium permanganate.

The process may be successfully applied to the estimation of not too small proportions of manganese in iron-spar and nickel-steel; also in "spiegeleisen" and ferromanganese. L. DE K.

**Volumetric Estimation of Iron.** By OTTO SCHMATOLLA (*Chem. Centr.*, 1901, ii, 1094; from *Pharm. Zeit.*, 1901, **46**, 810).—When reduced iron is tested by the process of the German Pharmacopœia, the addition of potassium iodide retards the solvent action of the iodine; the following modification is therefore proposed: 0.3 gram of the sample is put into a stoppered flask with 5—10 c.c. of water and 1.6 grams of coarsely powdered iodine, the flask is placed in cold water and frequently shaken until the iodine has dissolved. After remaining for half an hour at the ordinary temperature, the excess of iodine is titrated with  $N/10$  thiosulphate.

When pulverised iron is tested, the freshly prepared sulphuric acid solution should be diluted to 200 c.c. A portion is placed in a burette and slowly added to about 2 c.c. of a 2—3 per cent. solution of potassium permanganate until this is perfectly clear and decolorised. It is then mixed with iodine (? potassium iodide) and treated according to the Pharmacopœia process. L. DE K.

**Method of Quantitatively separating Nickel and Zinc.** By ARTHUR ROSENHEIM and ERNST HULDSCHINSKY (*Ber.*, 1901, **34**, 3913—3916. Compare Abstr., 1901, ii, 533).—Zinc forms a complex salt with ammonium thiocyanate,  $(\text{NH}_4)_2\text{Zn}(\text{SCN})_4 \cdot 4\text{H}_2\text{O}$ , which crystallises in white needles readily soluble in cold water; it closely resembles the corresponding cobalt compound (*loc. cit.*), and like the latter is insoluble in a mixture of ether and amyl alcohol. This property is used to separate zinc from nickel for the purposes of

quantitative estimation of a mixture of the two metals. The details of the process are similar to those previously described in the separation of nickel and cobalt (*loc. cit.*). Alloys of copper, zinc, and nickel, argentan, nickellin, and german silver, have been analysed by this process and the results compared with those obtained by the usual method; the agreement is very good.

K. J. P. O.

[Detection of Olefines in Light Petroleum.] By LUIGI BALBIANO and V. PAOLINI (*Chem. Zeit.*, 1901, 25, 932—933).—Two or three c.c. of the rectified sample boiling below 100° are shaken for 2 to 3 minutes with 10—12 c.c. of a cold saturated solution of mercuric acetate and then set aside in a closed tube for 24 to 36 hours. If then the aqueous liquid is turbid from the presence of small, white, lustrous lamellæ, the presence of an olefine is proved. The aqueous layer may contain aldehydes or ketones; processes are given for their identification.

L. DE K.

Determination of the Refractive Index of Ethereal Oils. By F. URZ (*Chem. Centr.*, 1900, ii, 1130; from *Apoth. Zeit.*, 16, 742—746).—The author used for his recent determinations an Abbé refractometer with prisms that can be heated. It became necessary to ascertain whether the index-division shown on the sector, which is calculated for the ordinary temperature, is available for higher temperatures; it appears that a correction is only requisite when the temperature exceeds 50°, but, considering the other sources of error, this is not of much practical interest. The same may be said about the increase of the dispersion of the glass with increase in temperature. However, at every observation the temperature should be recorded. The refractive index of a large number of ethereal oils is given for 15°, 20°, 25°, and 30°, and also the degree of dispersion at 15°. As a result of this investigation, the author has somewhat modified his previous view that the refractive index may serve to distinguish oils free from terpenes from the ordinary ethereal oils. This is only true in the case of a comparatively small number of ethereal oils, for instance, oils of lemon, fennel, juniper, sassafras, &c. The determination of the refractive index may, however, give a valuable clue as to the age of the oil, as it increases by long keeping; it will detect admixture of foreign ingredients if these possess a different refractive index from that of the oil and it will often tell the particular part of the plant from which the oil has been prepared.

L. DE K.

Detection and Decomposition of Iodoform. By C. H. L. SCHMIDT (*Chem. Centr.*, 1901, ii, 1095; from *Arch. internat. Pharm. Therap.*, 1901, 8, 110).—A starch solution, coloured blue by the presence of iodine, is mixed with dilute sulphuric acid and filtered from the iodide of starch. The filtrate is mixed with nitrite, which will then show the presence of hydriodic acid. Any precipitate is collected, and the filtrate mixed with zinc dust, which decomposes the iodoform and causes a further blue precipitate. By means of this reaction the author has found that iodoform gives off iodine at 100° and even at 80° in the presence of air; in the presence of water or

glycerol and air, part of the iodine is converted into hydriodic acid. Besides iodine, some carbon dioxide and carbon monoxide are also formed. The presence of the latter may be proved by heating the iodoform at  $100^{\circ}$  in a current of air and passing the vapours first through water and then through blood.

L. DE K.

**Detection of Iodoform in the Presence of some Organic Iodine Compounds.** By C. H. L. SCHMIDT (*Chem. Centr.*, 1901, ii, 1095; from *Arch. internat. Pharm. Therap.*, 1901, 8, 187).—In the presence of isopropyl iodide, allyl iodide, or di-iodohydrin, iodoform may be detected by taking advantage of the fact that, like allyl iodide, it may be decomposed or extracted by mercury or chloroform, whilst isopropyl iodide is only extracted by chloroform, and di-iodohydrin is neither decomposed by mercury nor extracted by chloroform. The presence of albumin does not interfere with the reaction. When iodoform, suspended in glycerol, is heated for a long time at  $100^{\circ}$ , carbon monoxide and carbon dioxide are evolved and the liquid contains free iodine, hydriodic acid, and traces of isopropyl iodide. The latter is formed by the action of hydriodic acid on the allyl iodide, obtained by the action of iodine on glycerol. Allyl iodide is only temporarily present in the liquid and may be detected by its odour and physiological action.

L. DE K.

**Detection of Methyl Alcohol in Ethyl Alcohol.** By JOSEF HABERMANN and A. OESTERREICHER (*Zeit. anal. Chem.*, 1901, 40, 721—724).—The method is based on the fact that an alkaline solution of potassium permanganate is decolorised much more rapidly by methyl alcohol than by ethyl alcohol. To 10 c.c. of the liquid to be tested, which must contain nothing except water and the respective alcohols (10 per cent.), two drops of a 10 per cent. solution of potassium hydroxide, and then one or two drops of  $N/10$  permanganate are added. With ethyl alcohol, the colour takes about 5 minutes to pass through violet and green to yellow, the green stage lasting for several minutes; if methyl alcohol is present, however, the change to yellow is so rapid that the intermediate colours can scarcely be observed. Liquids containing less than 5 per cent. of methyl alcohol require a preliminary fractional distillation.

M. J. S.

**Detection and Estimation of Methyl Alcohol in Commercial Formaldehyde.** By MAURICE DUYK (*Ann. Chim. anal. appl.*, 1901, 6, 407—409).—One hundred c.c. of the sample previously diluted with half its bulk of water are placed in a cooled flask and ammonia is slowly added in slight excess; if after a few hours the liquid still does not react with phenolphthalein, a little more ammonia should be added. A little sodium carbonate is added in order to render the hexamethylenetetramine more stable and the liquid is distilled until 100 c.c. have passed over. The distillate is neutralised with dilute sulphuric acid and redistilled in a bulb apparatus, and the fractions passing over between  $65^{\circ}$  and  $100^{\circ}$  are collected. These are again rectified so as to obtain a distillate containing three-fourths of its bulk of methyl alcohol. The methyl alcohol is finally estimated by converting it

into methyl iodide. For every 5 c.c., 10 grams of iodine and 2 grams of amorphous phosphorus are added; after a few hours the mixture is heated in a reflux apparatus and the whole distilled. The methyl iodide is collected in a graduated measure over water and from its volume that of the methyl alcohol is calculated. Commercial samples of formaldehyde have been found to contain from 3 to 10 per cent. of methyl alcohol.

L. DE K.

**Estimation of Glycerol.** By SIMON ZEISEL and R. FANTO (*Chem. Centr.*, 1901, ii, 1131; from *Zeit. landw. Versuchs-Wes. Oesterr.*, 4, 977—979).—The glycerol is boiled in a reflux apparatus with hydriodic acid (b. p. 127°), which soon converts it into isopropyl iodide. This may then be distilled and its iodine estimated by means of Zeisel's alcoholic solution of silver nitrate.

L. DE K.

**Quantitative Separation of Cholesterols from Fats.** By E. RITTER (*Chem. Zeit.*, 1901, 25, 872).—Fifty grams of fat are heated on the water-bath in a large porcelain basin with 100 c.c. of alcohol and a solution of 8 grams of sodium in 150 c.c. of 99 per cent alcohol. When the alcohol has volatilised, 75 grams of salt are added and then so much water that the greater part of the mass dissolves. The liquid is afterwards evaporated to dryness, first over the naked flame, then on the water-bath, and finally in a drying oven at 80°. The residue is finely powdered, put into a paper cartridge, and extracted with ether in a Soxhlet tube for 9 hours. Sand or paper cannot be substituted for the salt.

To remove traces of soap and glycerol, the ether is distilled, the residue dissolved in as little alcohol as possible, and reprecipitated by water. The cholesterol is collected on a filter and dried at 60°; the bulk of it is then transferred to a weighed flask and the last adhering particles are rinsed off with ether. The ether is evaporated and the residue dried at 100—120°.

L. DE K.

[**Estimation of Sugar in Beets.**] By R. S. HILTNER and R. W. THATCHER (*J. Amer. Chem. Soc.*, 1901, 23, 863—868).—A polemical reply to the criticism of Ewell (*J. Amer. Chem. Soc.*, 1901, 23, 432) on the method described by the authors for the estimation of sugar in beets (*Abstr.*, 1901, ii, 535).

E. G.

**Estimation of Volatile Acidity of Wines.** By XAVIER ROCQUES and G. SELLIER (*Ann. Chim. anal. appl.*, 1901, 6, 414—417).—The authors had previously devised (*ibid.*, 1898, 3, 222) an apparatus based on the same principle as that of Curtel (this vol., ii, 55). They think, however, that the sources of error mentioned by Curtel are not of sufficient importance notably to affect the results of the distillation process.

Another possible source of error, however, is that, if the wine should contain bisulphates and be concentrated to a very small volume, the tartaric acid will be acted on with formation of carbon dioxide and

an aldehyde which collects in the distillate and renders the titration slightly inaccurate. L. DE K.

**Estimation of Uric Acid.** By ADOLF JOLLES (*Zeit. physiol. Chem.*, 1901, 33, 542—546).—The author maintains, in opposition to Folin and Shaffer (*Abstr.*, 1901, ii, 585), that his method (*Abstr.*, 1900, ii, 450, 515) is accurate. W. D. H.

**Detection of Benzoic Acid and Alkali Benzoates in Food.** By J. DE BREVANS (*J. Pharm. Chim.*, 1901, [vi], 14, 438—440).—The sample to be tested is extracted with water (if a liquid, 200 c.c. are taken), the solution filtered, acidified with dilute sulphuric acid, and extracted three times with 50 c.c. of a mixture of equal volumes of ether and light petroleum. The residue left on evaporation of the ethereal solution may contain "saccharin," salicylic acid, and benzoic acid. If the first two are absent, the benzoic acid may be tested for in the following way. A small portion of the residue is placed in a dry test-tube, 2 c.c. of aniline containing 0.02 gram of rosaniline hydrochloride per 100 c.c. are added, and the mixture boiled for about 20 minutes, when, if benzoic acid is present, the liquid becomes red, then blue, and finally violet in colour. A few drops of dilute hydrochloric acid are next added, and the solid portion, which is now blue in colour, is collected, washed until all the violet colouring matter is removed, and finally dissolved in alcohol, when, if benzoic acid was originally present, the blue colour due to the aniline-blue formed is clearly seen. H. R. LE S.

**Application of Iodine Monobromide in the Analysis of Fats and Oils.** By JOS. HANUŠ (*Zeit. Nahr.-Genussm.*, 1901, 4, 913—920).—Iodine monobromide may be easily prepared by slowly adding 13 grams of bromine to 20 grams of powdered iodine with constant stirring, and cooling to 5—8°. The reaction takes about 10 minutes for completion and the product is freed from any uncombined bromine by passing a rapid current of carbon dioxide over it. It constitutes a grey, crystalline, metallic-looking substance which should be preserved in a stoppered bottle. The author prefers to use its solution in glacial acetic acid instead of the well-known Hübl solution for the following reasons. Its strength is readily ascertained by adding potassium iodide and titrating with sodium thiosulphate, it keeps for a considerable time and it acts on fats with great rapidity, so that an iodine absorption takes only 10—15 minutes. In practice, it has been found convenient to dissolve 10 grams of the compound in 500 c.c. of glacial acetic acid.

0.6—0.7 gram of solid fats, 0.2—0.25 gram of oils having an iodine figure below 120, or 0.1—0.15 gram of oils showing a higher figure is dissolved in a beaker or stoppered flask in 10 c.c. of chloroform and 25 c.c. of the standardised iodine monobromide solution are then added from a burette. After standing for 10 minutes (fats) or 15 minutes (oils), 15 c.c. of solution of potassium iodide (1 : 10) are added, and the liberated iodine titrated with sodium thiosulphate without using starch. The results agree with those of Hübl. L. DE K.

**Systematic Inspection of Milk for Preservatives.** By ALBERT E. LEACH (*Analyst*, 1901, 26, 289—291).—Formaldehyde is tested for by heating to boiling in a porcelain casserole 10 c.c. of the sample with 10 c.c. of hydrochloric acid containing 1 c.c. of 10 per cent. ferric chloride per 500 c.c. The presence of formaldehyde is indicated by a more or less intense violet coloration. Although objection has been taken to this test on account of other colour reactions taking place, the author has never met with a sample giving this reaction, where the presence of formaldehyde could not also be proved by other tests.

The ash obtained in due course is moistened with a drop or two of dilute hydrochloric acid, when any effervescence will show the presence of sodium carbonate; the original sample is examined by the rosolic acid test for carbonate. A few c.c. of water are then introduced into the crucible and when the ash is dissolved it is tested in the usual way for boric acid with turmeric paper.

L. DE K.

**Detection of Margarine in Butter.** By CHARLES ANNATÒ (*Chem. Centr.*, 1901, ii, 836; from *Pharm. Zeit.*, 46, 693).—The butter prepared from the milk of three cows, which, in addition to their usual food, had also partaken of sesamé cakes, gave with the furfuraldehyde test a decided reaction for sesamé oil. The mere fact of this test being obtained does not, therefore, prove the presence of margarine. On account of its liquid nature, sesamé oil itself cannot be employed as a butter adulterant, but only so when in combination with tallow or similar fats.

L. DE K.

**Detection of Margarine in Dairy Products by means of the Sesamé Oil Test.** By HERMANN BREMER (*Chem. Centr.*, 1901, ii, 955; from *Pharm. Zeit.*, 46, 757—758).—The author strongly doubts Annatò's statement that butter prepared from the milk of cows which have been fed on sesamé cake gives the furfuraldehyde test for sesamé oil, and suggests that the test has been improperly applied. It is of the utmost importance that the butter-fat should be carefully filtered, so as to remove every trace of casein. It is, however, thought possible that a chemical extraction of the milk might yield a fat giving the reaction.

L. DE K.

**Detection of Sesamé Oil.** By PAUL SOLTSIEN (*Chem. Centr.*, 1901, ii, 1095; from *Pharm. Zeit.*, 46, 771—772).—A reply to Bremer. Even now the author would prefer the sugar to the furfuraldehyde test if the use of the latter had not been made obligatory [in Germany]. The fact, stated by Schrott and Fiechtl, that a solution of furfuraldehyde in hydrochloric acid gradually turns red, had been noticed independently by the author.

L. DE K.

**The Sesamé Oil Reaction in Butter Analysis.** By CHARLES ANNATÒ (*Chem. Centr.*, 1901, ii, 1095—1096; from *Pharm. Zeit.*, 46, 772).—A reply to Bremer. The author was fully aware of the precautions to be taken to ensure a successful sesamé oil reaction.

L. DE K.

**Detection of Margarine by means of the Sesamé Oil Reaction.** By HERMANN BREMER (*Chem. Centr.*, 1901, ii, 1096; from *Pharm. Zeit.*, 46, 818—819. Compare Abstr., 1900, ii, 325).—A reply to Soltsien and Annatò (preceding abstracts). L. DE K.

**Is the Sesamé Oil Reaction of a Butter a sufficient Proof of Adulteration.** By A. REINSCH (*Chem. Centr.*, 1901, ii, 1096; from *Milch. Zeit.*, 30, 643—644).—In the author's experience, every sample of butter which gave the sesamé oil reaction was found to contain margarine. Undoubtedly genuine butter never gave the reaction. It is a matter of regret that the feeding experiments of Vieth and Siegfeld have not been carefully repeated. L. DE K.

**Detection of Sesame Oil.** By FERNAND RANWEZ (*Rev. intern. Falsif.*, 1901, 14, 125—127).—Soltsien has stated that the test with hydrochloric acid and furfuraldehyde is untrustworthy and has recommended the use of a solution of stannous chloride instead. The author states that the latter test is not delicate enough for the detection of small quantities of sesame oil in butter, and has also proved by a number of experiments that the furfuraldehyde test may be safely used. In the absence of sesame oil, no colour is developed for several hours and only on a prolonged contact is a brownish-yellow coloration gradually formed; this is not likely to be mistaken for the red colour caused by sesame oil. L. DE K.

**Occurrence and Detection of Sesamé Oil in Commercial Arachis Oils.** By PAUL SOLTSIEN (*Chem. Revue*, 1901, 8, 202—203).—Tampon has stated that the fatty acids obtained from arachis oil, give, like sesame oil, the Baudouin furfuraldehyde reaction. The author has fully investigated this matter and states that there is hardly any commercial arachis oil which does not contain sesame oil either by actual adulteration or from the fact that often arachis oil is pressed after sesame oil. Samples prepared by the author never gave the reaction.

When applying Baudouin's test to the fatty acids, it must be borne in mind that the active principle of sesame oil is somewhat soluble in mineral acids and, in consequence, gets partly removed; however, the presence of 1 per cent. of sesame oil in arachis oil may be safely detected when operating with the fatty acids; stannous chloride should not be substituted for furfuraldehyde as it causes the fatty acids to turn brown. L. DE K.

**Some Analyses of Bulgarian Butter derived from Buffaloes and Sheep, also of Bulgarian Lard and Walnut Oil.** By NIKOLAUS PETKOW (*Zeit. Nahr.-Genussm.*, 1901, 4, 826—828).—Analyses are given of fourteen samples of buffalo and 12 samples of sheep's butter, showing the amount of water, fat, non-fatty matters, sp. gr. of the fat at 100°, refraction, Reichert-Meißl number, Köttstorfer number, iodine number, insoluble fatty acids, and free acids (Burstyn's method). Both varieties of butter show no practical difference from cow's butter except in so far that the Reichert-Meißl numbers of the buffalo butter were higher than in mostly the case with cow's butter; they varied from 31.02 to 38.2.

Similar analyses of three samples of Bulgarian lard showed that this does not materially differ from other European lard. The average analysis of 5 samples of cold-pressed Bulgarian walnut oil gave: sp. gr. 0.9258, at 15°: refractometer number 67.7, at 40°: iodine number 148.21 and acidity (Burstyn) 4.38. L. DE K.

**A Sharp Indicator for Titrating Dark Coloured Fats.** By J. FREUNDLICH (*Chem. Centr.*, 1901, ii, 1094—1095; from *Oesterr. Chem. Zeit.*, 1901, 4, 441—442. Compare *Abstr.*, 1900, ii, 41).—When phenolphthalein cannot be used as an indicator, the author recommends that for each titration 10 c.c. of a 2 per cent alcoholic solution of Alkali Blue II OLA should be used. L. DE K.

**New Gravimetric Estimation of Formaldehyde.** By LUDWIG VANINO (*Zeit. anal. Chem.*, 1901, 40, 720—721).—When added to a mixture of silver nitrate with an excess of sodium hydroxide, formaldehyde is oxidised to sodium formate with reduction of a corresponding amount of silver oxide to the metallic state. After being left for 15 minutes in the cold, secluded from light, the precipitate is digested three or four times with an excess of 5 per cent. acetic acid. This dissolves the unreduced silver oxide and the reduced metal can then be collected on a weighed filter, washed, dried, and weighed. M. J. S.

**Microchemical Examination of Tea and Observations on Caffeine.** By P. KLEY (*Rec. Trav. Chim.*, 1901, 20, [ii], 344—351).—About one-third of a tea leaf is mixed with an equal quantity of quicklime and of water, dried at 100°, and moistened with two to three drops of alcohol in a small filtering tube. The filtered solution is evaporated, the residue placed on a small mica plate, surrounded by a ring of asbestos and sublimed on to a glass cover slip. The sublimate generally consists of an amorphous centre with radiating needles; if the latter do not show, the plate is breathed on after drawing across it a platinum wire with which a crystal of caffeine has been broken. The whole of the amorphous mass gradually becomes crystalline. Tea leaves which have once been extracted do not give a sublimate of caffeine under these conditions.

On crystallising caffeine from water at 70°, short, thick needles are obtained with a rectangular extinction between crossed nicols, which are totally different from those of ordinary caffeine, the extinction of which is at 36°; the former crystals are anhydrous, the latter hydrated.

On subliming anhydrous caffeine to which a little water has been added, anhydrous crystals are deposited, unless the surface of deposition has upon it a trace of the hydrated substance; when this is present, the sublimate is hydrated. Hydrated caffeine loses the whole of its water over sulphuric acid. W. A. D.

**Detection of Nicotine by means of Formaldehyde.** By SCHINDELMEISTER (*Rev. intern. Falsif.*, 1901, 14, 129).—If a trace of nicotine is mixed with 1 drop of 30 per cent. formaldehyde, a solid residue is formed after some hours which gives an intense rose color-



tion when touched with a drop of strong nitric acid ; if resinous matter is present, a blood-red colour appears. After some time, the colour changes to green. A more permanent colour is obtained when instead of formaldehyde pure formic acid is used. The test is characteristic for nicotine and is not given by conicine and similar organic bases formed by putrefying meat.

L. DE K.

**Analysis of Raspberry Juice.** By EDUARD SPAETH (*Zeit. Nahr.-Genussm.*, 1901, 4, 920—930) (continued from Abstr., 1901, ii, 291).—Full details are given for the detection of sugar substitutes (starch-syrup, "saccharin," dulcin), preservatives (salicylic acid, benzoic acid, calcium  $\beta$ -naphtholsulphonate [abastrol], alcohol, boric acid), organic acids, and esters by already known processes.

Raspberry juice, or syrup, when pure, is characterised by freedom from unfermentable polarising substances (dextrin) after treating the fermented solution with basic lead acetate, and also by the fact that the fixed acidity is mainly due to malic acid. The author also observes that the test for artificial colours as laid down in the German Pharmacopœia, namely, agitation with amyl alcohol, is not conclusive, but that it should be supplemented by the "wool test" and the usual tests for vegetable colours.

L. DE K.

**Estimation of the Alkalinity of Blood.** By AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and HENRI BARBIER (*Compt. rend.*, 1901, 133, 692—695).—The various methods of estimating the alkalinity of blood yield variable results, and the authors find that greater accuracy is secured if, after mixing the blood with excess of acid, the residual acid is determined by causing it to act on a mixture of potassium iodate and iodide and titrating the liberated iodine. With a constant quantity of acid and varying quantities of blood, however, the alkalinity decreases as the quantity of blood increases, but constant results are obtained if the quantity of acid added is proportional to the weight of blood taken. The alkalinity as thus determined represents the true alkalinity and a fraction of the total basicity of the blood.

C. H. B.

**Detection of Peptone in Urine.** By ZDENKO ČERNÝ (*Zeit. anal. Chem.*, 1901, 40, 592—595).—Urine is commonly examined for peptone either by saturating with ammonium sulphate or by precipitating with phosphotungstic acid and testing either precipitate for the biuret reaction. From urine rich in urobilin, that substance is also precipitated by both reagents, and likewise gives the biuret reaction. Bang has shown that the ammonium sulphate precipitate can be freed from urobilin by washing with alcohol. The author finds that if the phosphotungstic acid precipitate of urobilin is decomposed by barium hydroxide and the warm alkaline solution shaken with air, the urobilin becomes oxidised, with the possible exception of traces which are too small to produce the biuret reaction. The phosphotungstic precipitate obtained by Hofmeister's method is more easily oxidised than that prepared by Salkowski's method.

M. J. S.

## General and Physical Chemistry.

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**Dispersion of Ultra-violet Rays.** By F. F. MARTENS (*Ann. Phys.*, 1901, [iv], 6, 603—640).—A theoretical and physical paper, not suitable for abstraction. J. C. P.

**Radioactivity of Uranium** By HENRI BECQUEREL (*Compt. rend.*, 1901, 133, 977—980).—The author has previously found (*Abstr.*, 1900, ii, 518) that if solutions of uranium compounds are mixed with a small quantity of a barium salt and the latter is precipitated, the radioactivity of the precipitate is considerably higher than that of the original uranium compound, whilst by several repetitions of this process the radioactivity of the uranium compound is greatly reduced. After the expiration of eighteen months, he has again examined the various products and finds that the uranium preparations have regained their original radioactivity, with practically the same intensity in all cases, whereas the barium precipitates have entirely lost their radioactivity, or, in other words, have behaved as if their very marked radioactivity was simply induced. The author considers that these results show that uranium compounds have a radioactivity of their own, although the possibility that the uranium may contain a small quantity of some specially radioactive substance not separated in the various operations is not excluded. The recovery of radioactivity is in all probability a phenomenon of auto-induction, and supports the author's view that the emission of rays not deviated in a magnetic field is due to the emission, by the same substance, of deviable rays, just as Rontgen rays are produced by the impact of cathode rays. The author has repeated his observations on the radioactivity of uranium compounds at the temperature of liquid air, and confirms his previous result. C. H. B.

**Researches on Contact Electricity.** By OSCAR KNOBLAUCH (*Zeit. physikal. Chem.*, 1901, 39, 225—244).—The author determined the sign of the charge left on plates of platinum, paraffin, glass, and sulphur, on the removal of various powders which had been placed on the plates. Seventy-five different compounds were employed, including acids, bases, neutral salts, and various organic products. Platinum and paraffin become positively charged if the powder is of an acid nature, negatively if it is alkaline, whilst for neutral compounds the charge left is sometimes positive, sometimes negative. Sulphur becomes positively charged by contact with acid powders, but negatively in almost all other cases; glass, however, becomes negatively charged, except when the powder is of an alkaline nature. These results are satisfactorily explained on the assumption that plates and powders are coated with a film of the saturated aqueous solution; when an acid powder is placed on the platinum or paraffin plate and the films are hence in contact, the hydrogen ions, on account of their greater velocity, pass in excess into the platinum surface film, so that when

the powder is removed, the plate is positively charged. Similar reasoning explains the negative charge with alkaline powders, whilst in the case of neutral salts, the charge is dependent on the relative velocities of the two ions. The differences between the results obtained with glass and sulphur plates are due to the fact that the films on the plates themselves are respectively alkaline and acid solutions. The author further discusses the law enunciated by Cœhn that, of two dielectrics in contact, the one with the higher dielectric constant becomes positively charged (Abstr., 1898, ii, 365).

L. M. J.

**The Discharge Potential of Hydrogen at a Mercury Cathode.** By ALFRED COEHN and EDGAR NEUMANN (*Zeit. physikal. Chem.*, 1901, **39**, 353—354).—The difference between the discharge potential of hydrogen at a platinum and at a mercury cathode at  $-85^{\circ}$  is nearly the same as the difference at  $18^{\circ}$ , and the authors conclude that, since in one case the mercury is solid and in the other case it is liquid, the discharge potential of hydrogen at metal cathodes is dependent, not on accidental properties of the metal, such as the form and nature of the surface, but on the chemical individuality of the metal.

J. McC.

**Potential Differences in Vapours and in some Solid Electrolytes.** By RUDOLF VON HASSLINGER (*Monatsh.*, 1901, **22**, 907—916).—The author has measured the potential differences assumed by metals when placed in a bunsen burner into which solutions of various salts are sprayed. The potential difference is influenced by the basic as well as the acid constituent of the salt, but the greater part of the potential difference measured seems to be due to the latter. The most remarkable result observed was that, in the vapour of certain salts, iron and nickel assumed a positive potential towards platinum. In fused lithium chloride, iron is negative towards platinum. The difference of potential varies with the temperature, the maximum value being reached at about  $800^{\circ}$ . On further raising of the temperature, the *E.M.F.* decreases, and in lithium chloride, vapour passes through zero to the change of sign.

The same phenomenon is well-shown with the solid electrolytes, calcium and magnesium oxides.

G. Y.

**Dielectric Constant of Paraffins.** By WILL G. HORMELL (*Amer. J. Sci.*, 1901, [iv], **12**, 433—446).—The paper is mainly physical. By means of an electric wave method, the author finds that the higher the melting point of the paraffin, the greater is the dielectric constant. As the wave-length diminishes, the dielectric constant increases. Cauchy's formula for calculating the index of refraction for infinitely long waves gives results inconsistent with experiment.

J. C. P.

**Electrical Properties of Alloys of Copper and Cobalt.** By G. REICHARDT (*Ann. Phys.*, 1901, [iv], **6**, 832—855).—The effect of small quantities of cobalt on the electrical properties of copper is almost as great as that of manganese and about three times as great as that

of nickel. The addition of 3—5 per cent. of cobalt gives an alloy with a minimum temperature coefficient of resistance ( $+0.00077$ ), and with a maximum thermoelectric effect (against copper) of 33 microvolts for  $1^{\circ}$  temperature difference. Up to this composition, the specific resistance of the alloys increases rapidly, but further addition of cobalt produces only a slow increase of resistance. The only practical application that could be made of the alloys is in the construction of thermoelectric batteries.

The addition of small quantities of copper has a great effect on the properties of cobalt. The specific resistance has a maximum, the thermoelectric effect a minimum, value between 0 and 10 per cent. of copper. All alloys except those containing less than 1.5 per cent. of cobalt can be magnetised, the magnetism being destroyed only at a bright-red heat. It is noted that alloys of copper and nickel cannot be magnetised.

J. C. P.

**Electrical Conductivity of Flames and Gases.** By ALEXANDRE DE HEMPTINNE (*Zeit. physikal. Chem.*, 1901, 39, 345—352. Compare Abstr., 1893, ii, 563).—The deflection of a galvanometer needle contained in a battery circuit was observed when gas explosion took place in a tube containing free ends (electrodes) of the circuit. The deflection decreases with decrease of *E.M.F.* of the battery, but not exactly proportionally. It decreases as the distance between the electrodes is increased. When the electrode connected with the positive pole of the battery is large and that connected with the negative pole is small, a large deflection is obtained, whilst if the connections be reversed only a small deflection is noticed, thus indicating that the conductivity of an explosion (like that of a flame) is unipolar. The deflection is greatest when the explosion tube is open to the air, and is very small when the whole apparatus is kept at a temperature much above  $100^{\circ}$ . Practically the same results were obtained when the electrodes consisted of platinum, gold, or iron wires, and a magnetic field is also without influence. These experiments were made with an explosive mixture of hydrogen and oxygen. With a dry mixture of hydrogen and chlorine, or of oxygen and carbon monoxide, no deflection was obtained, but when the mixture was moist, the needle moved through 0.5 mm. From the experiments, it is deduced that no ions take part in the gas reaction, but the electricity is solely transported by condensed water, for conditions under which condensation may take place favour the transportation.

J. McC.

**A Peculiar Cell containing Chromic Chloride (Electrochemical Equilibrium between Different Degrees of Oxidation).** By ARRIGO MAZZUCHELLI (*Gazzetta*, 1901, 31, ii, 371—395).—In 1886, Case described a cell (*Proc. Roy. Soc.*, 1886, 40, 348) consisting of tin and platinum poles in chromic chloride solution, which he stated had an *E.M.F.* 0 at the ordinary temperature, and 0.25 volt at  $95^{\circ}$ . It was found later, however, by Skinner (Abstr., 1896, ii, 3), that this cell has the *E.M.F.* 0.44 volt at  $15^{\circ}$  and 0.40 volt at  $97^{\circ}$ , but that it polarises much more readily at low than at higher temperatures. The reactions taking place in the cell are, at high temper-

atures, the solution of tin by the liquid with the production of chromous chloride, and reprecipitation of the tin in the cold. As was shown by Case, the cell is very variable in its action; the *E.M.F.* is altered by shaking and exhibits a steady decrease when the cell is left to itself on open circuit, the fall being more rapid at high than at lower temperatures. The author explains these changes as due in the first instance to the action of the chromic chloride on tin, which takes place as a local action, even when the cell is an open circuit, producing stannous and chromous chlorides; the latter are then always present in the liquid of the cell in proportions depending on the amount of surface presented by the tin, on the time of standing, &c., and further, their distribution throughout the liquid is not uniform. The potential of the platinum is, of course, dependent on the exact composition of the liquid in contact with it. The author derives, from theoretical considerations, the action of a cell containing both oxidising and reducing compounds, and endeavours to determine chemically the equilibrium between tin and chromic, chromous, and stannous chlorides, but the numbers obtained do not agree with the theoretical values. The only interest attaching to this cell is not, as was stated by Haber (*"Electrochemie,"* p. 177), that it allows of the direct transformation of heat into electrical energy, or, as was mentioned by Skinner, that it is capable of executing a Carnot's cycle, but that owing to the very high temperature coefficient of the reaction taking place in it, the chemical and electrical equilibria between the different states of oxidation are readily attained. T. H. P.

**The Decomposition-tension of Molten Sodium Hydroxide and of Lead Chloride.** By JULIUS FRIEDRICH SACHER (*Zeit. anorg. Chem.*, 1901, 28, 385—460).—When sodium hydroxide is fused in an iron vessel it soon assumes a red tinge, and when this has happened the iron has become passive so that on immersion of an iron wire into the fused mass there is no polarisation current; up to the time when this passive state has been induced, a polarisation current of very variable strength is obtained. The only metals suitable for electrodes in the electrolysis are iron and platinum, the former being preferable. The discharge potential and the cathodic and anodic decomposition-tensions of fused sodium hydroxide have been determined in an iron vessel with an iron electrode, and with a platinum vessel and electrode, at temperatures varying between 385° and 563°, and between 575° and 694°. The curve of cathodic decomposition shows two well-marked breaks, as also does that of the anodic decomposition; the values found for the points at which the curve shows a sudden change are: for the cathodic discharge, 1.16 volts (at 390°) and 2.06 volts (at 389°), and for the anodic, 0.11 volt (at 395°) and 1.31 volts (at 393°). The higher cathodic point corresponds with the separation of sodium and the lower with the separation of hydrogen. The higher anodic point is due to the discharge of hydroxyl ions and the lower to that of O' ions. This lower anodic point disappears as the hydroxide becomes free from water and the author concludes that the sodium hydroxide dissociates into Na· and OH', and the water either itself gives the ions H· and O'· or causes these to be formed from the OH'

The polarisation of fused lead chloride was determined by the decomposition method in glass vessels of various forms, using carbon electrodes. Two breaks occur in the curves obtained; the position of the lower break varies greatly with the distance between, and the size of the surface of, the electrodes. At  $575^{\circ}$ , the higher break occurs at 1.256 volts, at  $681^{\circ}$ , it is at 1.190 volts. When the electrodes are encased, the lower break entirely disappears. This lower break is due to a depolarisation effect produced by the depolarising action of a cloud of lead vapour which diffuses from the cathode to the anode. The higher break corresponds with the reversible action:  $\text{PbCl}_2 \rightleftharpoons \text{Pb} + \text{Cl}_2$ . Similar conclusions are to be drawn from the results obtained by determining the discharge potentials.

Considerable doubt must be entertained as to the interpretation of results given by Garrard (*Zeit. Elektrochem.*, 1899, 6, 214), who assumes that the electrolytic decomposition of salts of bivalent metals takes place in two stages:  $\text{MR}_2 = \text{MR} \cdot + \text{R}'$  (corresponding with the higher break in the decomposition curve) and  $\text{MR} \cdot = \text{M} \cdot + \text{R}'$  (corresponding with the lower break).  
J. McC.

**Influence of the Addition of a Salt with one similar Ion on the E.M.F. of Electrolytic Cells.** By OTTO SACKUR (*Zeit. physikal. Chem.*, 1901, 39, 364—368. Compare Abstr., 1901, ii, 636).—Planck's formula for the influence of a salt with one similar ion on the E.M.F. of an electrolytic cell becomes identical with that of Abegg and Bosc when the concentrations of the electrolyte,  $C_1$  and  $c_2$ , are the same.

It is shown that diffusion can take place against the fall of concentration, and that the ions do not only follow Dalton's law of partial pressure but their motion is influenced by osmotic and electrical forces.

J. McC.

**Electro-chemistry of Double Salts.** By WLADIMIR A. KISTIAKOWSKY (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 480—496 and 592—621).—The author indicates a new method of calculating the electrolytic potentials of the alkali and alkaline earth metals from the heats of formation of the haloid salts in dilute aqueous solution. The numbers given, which are calculated from results obtained by Thomsen and by Berthelot and refer to the potential of the hydrogen electrode in a normal solution taken as zero, differ from those of Wilsmore (Abstr., 1901, ii, 2).

The conditions of concentration and temperature necessary for the formation of the two complex salts,  $\text{Ag}_3\text{I}(\text{NO}_3)_2$  and  $\text{Ag}_2\text{INO}_3$ , have been investigated (compare Hellwig, Abstr., 1900, ii, 723). By measurements of the electromotive force of the concentration-cell,  $\text{Ag} | \text{AgNO}_3, \text{AgI} | \text{AgNO}_3 \text{ (concentrated)} | \text{AgNO}_3 | \text{Ag}$ , the author shows that the salt  $\text{Ag}_3\text{I}(\text{NO}_3)_2$  is resolved into the ions  $\text{Ag}_3\text{I}$  and  $2\text{NO}_3$ . In the case of  $\text{Ag}_2\text{INO}_3$ , the ions are probably  $\text{Ag}_2\text{I}$  and  $\text{NO}_3$ .

A relative measure of the free energy of formation of double salts of potassium cyanide with other cyanides has been obtained by determining the electromotive force of the element,  $\text{R} | \text{KCN} | \text{RX} | \text{R}$ , R being a metal and RX one of its salts. Where R represents Mg, Al, Zn, Cd, H, or Cu, it is found that the electromotive force increases as

the electro-affinity decreases, as is required by the principle put forward by Abegg and Bodländer (Abstr., 1899, ii, 542). The exceptions to this rule, namely, Ni, Pb, Hg, and Ag, are due to the capacity possessed by these elements for forming complex cathions.

The author has determined experimentally the relative velocities of migration of the ions of the double salts,  $\text{Ag}_3\text{Cr}(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$ ,  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ , and  $\text{K}_3\text{Co}(\text{CN})_6$ , the results showing that Kohlrausch's law holds for such complex salts. A sketch and description of the special apparatus employed in these measurements are given.

Measurements have also been made of the electrical conductivity of very dilute solutions of the salts,  $\text{KAg}(\text{CN})_2$ ,  $\text{K}_2\text{Ni}(\text{CN})_4$ ,  $\text{K}_3\text{Co}(\text{CN})_6$ ,  $\text{K}_3\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ , and  $\text{K}_3\text{Cr}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$ . T. H. P.

**Production and Maintenance of Low Temperatures.** By ARSÈNE D'ARSONVAL (*Compt. rend.*, 1901, 133, 980—983).—Temperatures down to  $-60^\circ$  are readily obtained by means of methyl chloride contained in a porous battery cell from the walls of which the necessary evaporation takes place spontaneously. Temperatures of  $-112^\circ$  to  $-115^\circ$  are obtained by means of solid acetylene or solid carbon dioxide, the former being as manageable as the latter, whilst it evaporates more slowly and at a lower temperature,  $-85^\circ$ . Both dissolve readily in acetone and the temperatures specified are produced by the evaporation of these solutions, the air which is bubbled through the liquid being previously cooled by passing through a metal worm cooled by the gases escaping from the liquid. For temperatures below  $-115^\circ$ , liquid air must be used, and with its aid any low temperature down to  $-194^\circ$  can be obtained and kept constant. The object to be cooled is immersed in a bath of paraffin of low boiling point, the bath being cooled by allowing liquid air to drop into and evaporate from a small metal vessel placed in the paraffin at its surface. The temperature is controlled by the rate of flow of the liquid air, which can be regulated in various ways. In the cylindrical double-walled vessels with a vacuous space between and with silvered walls, the loss of liquid air at the ordinary temperature by spontaneous evaporation from a vessel of about 1000 c.c. capacity is only about 20 grams per hour. C. H. B.

**New Furnace Heated by the Oxyhydrogen Blowpipe.** By HENRI MOISSAN (*Ann. Chim. Phys.*, 1901, 24, [vii], 289—298).—This furnace consists of a cylindrical box of hydraulic lime, perforated concentrically through its cover and bottom. The oxyhydrogen blowpipe is introduced into the lower aperture and the products of combustion escape by the hole in the cover. The crucible is made of quicklime, or of graphite with a protective outer coating of quicklime and is supported on three quicklime prisms placed on the floor of the furnace. This apparatus is employed in melting refractory substances and differs from the furnace devised by Deville and Debray in being heated from below instead of from above. As the flame does not come into contact with the contents of the crucible, the furnace may be used for fusing oxidisable substances. G. T. M.

[**Thermodynamics of Concentrated Solutions.**] By J. J. VAN LAAR (*Zeit. physikal. Chem.*, 1901, 39, 342—344).—The author

considers that the deductions made by Schükareff (this vol., ii, 4) are founded on false premises and are quite worthless. Thus he assumes that  $\mu_1$  is only a function of  $m_1$ , and  $\mu_2$  is only a function of  $m_2$ , whereas it is well known that  $\mu_1$  and  $\mu_2$  are very complicated functions of  $T$ ,  $p$ ,  $m_1$ , and  $m_2$ , and known only for some few simple cases. Further, there can be no distinction between "determinate" and "undeterminate" potential as supposed by Schükareff. J. McC.

**Heat of Formation of Chlorine Hydrate.** By ROBERT DE FORCRAND (*Compt. rend.*, 1901, 133, 1304—1306).—Direct determinations of the heat of dissolution of chlorine hydrate, corrected for the uncombined water present, and the quantity of chlorine that it holds in solution, gave  $-15.63$  Cal. as the mean of three experiments, and hence  $\text{Cl}_2 \text{ gas} + n\text{H}_2\text{O liq.} = \text{Cl}_2, n\text{H}_2\text{O, sol.}$  develops  $+18.57$  Cal. The value of the heat of formation, calculated from the curves of dissociation representing the observations of Isambert, Roozeboom, and Le Chatelier respectively, is  $+18.16$  Cal. C. H. B.

**Investigations with the Micromanometer.** By A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 4, 163—169. Compare Abstr., 1900, ii, 388, 389, 708; 1901, ii, 304, 436).—With a slightly modified form of his manometer, the author has determined the decrease of vapour tension for solutions of sodium chloride, sulphuric acid, and potassium nitrate. In the first two cases, a minimum value of  $i$  is found near the concentrations  $0.45$  gram-mol. and  $0.1$  gram-mol. per 1000 grams of water respectively. With potassium nitrate, on the other hand, there is a regular decrease in the value of  $i$  up to the most concentrated solution investigated  $-0.93$  gram-mol. per 1000 grams of water. These results are in qualitative agreement with those obtained by the boiling point method. The author thinks that the existence of a minimum value of  $i$  for sodium chloride will be satisfactorily proved by the freezing point method also, although this is not the case as yet (see Raoult, Abstr., 1899, ii, 203; Chroustchhoff, Abstr., 1900, ii, 86; Kahlenberg, Abstr., 1900, ii, 540). In reference to Kahlenberg's recent paper (*loc. cit.*), the author, whilst admitting that the values of  $i$  deduced from the conductivity differ in general from those obtained by a non-electrical method, does not regard this as sufficient ground for rejecting Arrhenius' theory. It is probable that the conductivity is a correct measure of the dissociation, and that the different values given by other methods are due to the simultaneous occurrence (in moderately concentrated solutions) of ions and the products of polymerisation or association. J. C. P.

**Polymerisation of Inorganic Chloro-anhydrides.** By GIACOMO L. CIAMICIAN (*Atti Real. Accad. Lincei*, 1901, [v], 10, ii, 221—226).—The fact that the molecular weights obtained from ebullioscopic measurements of certain inorganic chloro-anhydrides seem to indicate polymerisation of these compounds has been explained by Oddo (this vol., ii, 6) as due to the volatility of the dissolved substances at the temperature of the boiling solution. On determining the value of the ratio,  $\alpha$ , of the concentrations of phosphorus oxychloride in the



vapour given off from a benzene solution and in the solution itself, and allowing for the volatilisation by multiplying the observed molecular weight by  $(1 - \alpha)$ , Oddo (*loc. cit.*) found that the numbers obtained still exceeded the true molecular weight. On repeating these experiments, however, the author finds for  $\alpha$  a mean value of 0.515, Oddo's numbers being 0.27, 0.31, and 0.27; correcting by means of the value 0.515, the experimental molecular weights agree well with the normal value.

T. H. P.

**New Methods for the Determination of Molecular Weights of Substances in Dilute Solution.** By GIOVANNI GUGLIELMO (*Atti Real. Accad. Lincei*, 1901, [v], 10, ii, 232—239).—All those methods used in hygrometry to determine the tension of the aqueous vapour of the air and the relation between this tension and that of saturated water vapour at the same temperature may be employed to measure the tensions of vapours in contact with (1) a solution, and (2) the pure solvent, and from these the molecular weight of the dissolved substance can be deduced. The author describes in detail three different methods of working, in all of which very simple apparatus is made use of. (1) In the first method, a layer about 1 cm. deep of the solution is placed in a small flask furnished with a stopper containing three holes, through two of which pass thermometers reaching to within 1 cm. of the surface of the liquid, the bulb of one being surrounded by two or three thicknesses of filter paper fastened to the thermometer; through the third hole passes a rod for stirring the liquid. When the solution is in the flask, the stopper is raised for a moment, and by means of a pipette the covered thermometer bulb is thoroughly moistened with the solvent; the stopper being replaced, the temperatures indicated by the two thermometers soon become constant and are read off. The molecular weight of the solute is given by the formula  $M = C.p/(t - t_1)$ ,  $p$  being the weight of the dissolved substance per 100 parts of the solvent,  $t$  and  $t_1$  the temperatures of the dry and wet thermometer bulbs respectively, and  $C$  a constant depending on the vapour pressure of the solvent, on the atmospheric pressure, and on the change of the latter per  $1^\circ$ ;  $C$  may be calculated from these magnitudes, but it is preferable to determine it experimentally by measurements made on a solution of a compound of known molecular weight. (2) In this method, no thermometer is needed, as the rate of evaporation, and hence the rate of cooling, of a rod or tube surrounded at its lower part by filter paper and moistened with the solvent, is measured by its loss in weight in a certain time when placed in the flask employed in the previous method. (3) The third method makes use of a wide-mouthed flask containing a little of the solution and fitted with a perforated stopper which carries a wide, nickelled tube, closed at the bottom and containing a little of the solvent; the top of this tube is closed by a trebly-bored stopper, through which pass a thermometer and a tube drawn out to a fine point at the bottom, both dipping in the liquid, and another shorter tube open at both ends. Air is caused to bubble through the solvent by means of the drawn-out tube, the evaporation thus produced serving to cool the nickelled tube, which acts as the essential part of a Regnault's hygrometer.

The practical details and precautions to be attended to in the working of these three methods are given. T. H. P.

**Volume and Density Changes in Liquids due to the Absorption of Gases.** By E. WENZEL (*Ann. Phys.*, 1901, [iv], 6, 520—532).—A form of dilatometer is described by which the changes referred to can be accurately determined. The liquid used in the investigation was water, and the gases absorbed were hydrogen, oxygen, carbon dioxide, sulphur dioxide, and ammonia. Following Ångström (*Abstr.*, 1882, 687; 1888, 401), and defining the absorption-dilatation coefficient ( $\delta$ ) as the relative increase of volume of the liquid caused by absorption of 1 c.c. of gas at 0° and 760 mm. pressure, the author finds that, in the case of hydrogen and oxygen, the values of  $\delta$  are nearly independent of the quantity of gas absorbed; in the case of carbon dioxide, the value of  $\delta$  diminishes at first, then becomes constant, and finally, when the water is nearly saturated with the gas, rises slightly. For sulphur dioxide, there is a steady rise, for ammonia a steady fall, in the value of  $\delta$ . The law, therefore, according to which the increase of volume is proportional to the quantity of gas absorbed, holds only for gases which are but slightly soluble. The specific gravities of the dissolved gases have been calculated with the help of  $\delta$ ; the values thus calculated are in each case much greater than the specific gravities of the liquefied gases.

J. C. P.

**A New Method for the Determination of the Surface Tension of Liquids.** By WILLIAM HENRY WHATMOUGH (*Zeit. physikal. Chem.*, 1901, 39, 129—193).—The method consists essentially in the determination of the pressure necessary for the formation of bubbles at the end of a capillary tube dipping into the liquid, the value being compared with that required with the same capillary in a liquid of known surface tension. The precautions necessary to ensure accuracy are investigated, and the results show that when these are observed the method is both speedy and accurate. In salt solutions, the surface tension is a linear function of the concentration, and the author finds that an equal increase of surface tension is produced by equivalent weights of chlorides of lithium, sodium, potassium, barium, strontium, and magnesium; the effect of ammonium chloride was, however, slightly less, whilst that of calcium chloride was greater. The effect of sulphates is less than that of chlorides, and the effect of nitrates slightly lower than that of sulphates. The author does not find that keeping for 24 hours produces any alteration of surface tension of a solution, a result not in accord with the early observations of Quincke (*Ann. Phys. Chem.*, 1877, 160, 337). A number of binary mixtures were examined and may be divided into classes. (1) Mixtures in which the surface tension could be directly calculated from the surface tensions of the components, as in the case of chloroform and ethyl ether, benzene and toluene. (2) Mixtures for which the surface tension is throughout less than the calculated value, as for water and acetic acid, ethyl ether and benzene, &c. (3) Mixtures in which a minimum value is attained, as in the cases of toluene and xylene, acetic acid and benzene, and others. (4) Mixtures in which a maximum value is found; the

only mixture of this class examined was that of sulphuric acid and water, the maximum being reached when the mixture contains 46 per cent. of the acid, and it is noteworthy that the compressibility reaches a minimum at the same composition. A number of liquid mixtures which form two phases were also examined, and, as expected, the differences in the surface tensions of the two phases decreased with rise of temperature, becoming *nil* at the critical point. Solutions of two salts gave results in accord with those calculated additively. Some ternary mixtures were examined, and curves are given representing the results.

L. M. J.

**Number of Ions in Metallo-ammonium Compounds.** By EMIL PETERSEN (*Zeit. physikal. Chem.*, 1901, 39, 249—252).—A reply to Werner's criticisms on the author's work (*Abstr.*, 1901, ii, 638).

L. M. J.

**Solvent and Dissociative Powers of Liquid Cyanogen and Liquid Hydrogen Cyanide.** By M. CENTNERSZWER (*Zeit. physikal. Chem.*, 1901, 39, 217—224, and *J. Russ. Phys. Chem. Soc.*, 1901, 33, 545—547, 547—549).—Liquid cyanogen has but slight solvent power, and it is shown that its dissociative power is likewise very small. Experiments with liquid hydrogen cyanide showed, however, that the salts examined (potassium iodide and trimethylsulphine iodide) were far more highly dissociated in this solvent than in water, a result in accord with the Nernst-Thompson rule connecting the dissociative power and the dielectric constant (compare Schlundt, *Abstr.*, 1901, ii, 299).

L. M. J.

**Boundaries between Polymorphism and Isomerism.** By RUDOLF WEGSCHEIDER (*Monatsh.*, 1901, 22, 917—938).—The theoretical distinction between polymorphism and isomerism is held to be useful in spite of the vagueness of the dividing line. Polymorphism may occur along with polymerism as well as with isomerism.

A detailed discussion of the criteria by which these may be distinguished leads to the conclusion that, whereas isomerism may be sharply characterised, it is not possible to determine the presence of polymerism to the complete exclusion of isomerism (compare Schaum, *Abstr.*, 1898, ii, 372; Bancroft, *Abstr.*, 1899, ii, 145).

G. Y.

**Velocity of Reaction in Organic Solvents. Decomposition of Chloro- and Bromo-acetic Acids by various Bases in Solution in different Alcohols.** By A. SCHWEINBERGER (*Gazzetta*, 1901, 31, ii, 321—333).—The following table gives the mean values of *K* for the hydrolysis by means of different bases of bromoacetic acid dissolved in various alcohols and in water, the temperature in each case being 60°.

It will be seen that methyl alcohol acts irregularly, since in some cases it gives a quicker, and in others a slower, reaction than is obtained with ethyl alcohol. Further, in ethyl alcoholic solution, sodium methoxide has a less rapid hydrolysing action than the ethoxide, whilst from a consideration of the dissociation in the two cases, the contrary would be expected. This anomalous behaviour of methyl

Base	Water.	Alcohols.		
		Ethyl.	Methyl.	Propyl.
Sodium hydroxide.....	0.82	0.75	0.54	—
Potassium „ .....	0.98	0.70	0.596	—
Sodium methoxide.....	—	0.32	0.59	1.7
Sodium ethoxide .....	—	0.37	0.54	—
Sodium propoxide.....	—	0.55	0.39	—
Ammonia .....	2.3	0.75	0.326	—

alcohol has been noticed in other reactions by various observers, and may be explained as due to some kind of chemical action taking place between the solvent and the solute, and influencing the general relations of the solvent as predicted from its physical properties.

T. H. P.

**Law of the Action of Invertase.** By VICTOR HENRI (*Zeit. physikal. Chem.*, 1901, 39, 194—216; *Compt. rend.*, 1901, 133, 891—894).—The velocity of inversion of sucrose by invertase is not represented by the equation  $dx/dt = k(a - x)$  leading to  $k = l/t[\log a/(a - x)]$ , but the author shows that the reaction velocity may be expressed by  $dx/dt = k_1(1 + x/a)(a - x)$  or  $2k_1 = l/t[\log(a + x)/(a - x)]$ . Experiments were also made in which, after various intervals of time, additional quantities of sucrose were added to the solution undergoing inversion by diastase, and it was found that time had no effect on the activity of diastase, the velocity depending only on the concentrations of  $a$  and  $x$ . The value of  $k_1$  varies with the initial concentration, but the value  $ka$ , is not constant; it increases with  $a$  at low concentrations, attaining a maximum at from 0.1  $N$  to 0.4  $N$  solutions (Abstr., 1901, i, 438; ii, 647).

L. M. J.

**Pseudocatalytic carrying of Oxygen.** By CARL ENGLER and LOTHAR WÖHLER (*Zeit. anorg. Chem.*, 1901, 29, 1—21. Compare Abstr., 1897, ii, 402; 1899, i, 189, 221; 1900, i, 399; 1901, i, 657).—Pseudocatalysis (Wagner, Abstr., 1899, ii, 275), in which oxidation takes place, can be divided into three categories where the oxygen carrier is (1) a noble metal or its easily reducible oxide, (2) an oxide or salt of an element the valency of which varies, (3) an animal or plant oxidation-ferment.

The results of Mond, Ramsay, and Shields (Abstr., 1895, ii, 492; 1898, ii, 599) on the occlusion of oxygen by platinum black have been confirmed and the following facts also observed. Platinum black turns potassium iodide starch solution blue; it is somewhat soluble in dilute hydrochloric acid, the weight of platinum in solution is less than the weight of platinum black dissolved, and if the difference be attributed to oxygen it is found that the ratio of platinum to oxygen agrees well with  $PtO$ ; the amount of oxide present in the platinum sponge depends on the state of division. It does not easily amalgamate,

and the amalgam formed becomes covered with a film of the black oxide; hydrogen peroxide does not reduce it in the cold, but on boiling, complete reduction takes place, and it is also reduced by alcohol, ether, and other organic substances; in absence of air, it oxidises arsenious to arsenic acid, and the residue loses its spongy character and becomes granular. It is further shown that the properties of active platinum sponge closely resemble those of platinous oxide, in confirmation of the theory of de la Rive that in the catalysis by platinum black, the intermediate active agent is this oxide. However, platinum sponge free from oxide causes more active oxidation than does platinous oxide, and this is explained by the Engler-Wild theory (Abstr., 1897, ii, 402) of the intermediate formation of peroxide and secondary formation of oxide, which takes place more readily with the finely divided sponge than with the more compact platinous oxide.

In like manner, the authors attribute the solution of gold in potassium cyanide in presence of oxygen to the formation of gold peroxide, which dissolves as expressed by the equation  $\text{Au}_2\text{O}_2 + 4\text{KCN} = 2\text{KAu}(\text{CN})_2 + \text{K}_2\text{O}_2$ .

Pseudocatalysis by means of oxides or salts of chromium, iron, cobalt, nickel, copper, mercury, and, in a less degree, by those of titanium, zirconium, cerium, thorium, tin, and molybdenum, and even by the non-metals phosphorus and carbon, is also explained by the intermediate formation of peroxide.

Catalysis in the plant and animal world is also due to formation of peroxides, and analogies are drawn between the oxidation-ferments and platinum sponge.

J. McC.

**The Solution Theory of Dyeing.** By REGINALD B. BROWN and JOHN McCRAE (*J. Soc. Chem. Ind.*, 1901, 20, 1092—1093. Compare Abstr., 1901, i, 99; *Trans.*, 1896, 1334; *J. Soc. Chem. Ind.*, 1901, 20, 226).—The authors conclude from their experiments that within wide limits of concentration a constant percentage of dye is taken up by wool, when the relative amounts of wool and water, the temperature, and the duration of the experiment are constant. The authors favour the view that in certain cases the operation of dyeing consists simply in the formation of a solid solution, and to this solution Henry's law is strictly applicable, but at the same time they recognise that this does not hold good in general, for the non-reversibility of the process in most cases favours the view that a chemical or physical change takes place during the fixing.

H. R. LE S.

**Colloids.** By GRÉGOIRE WYROUBOFF (*Bull. Soc. Chim.*, 1901, [iii], 25, 1016—1022).—A controversial paper, not suitable for abstraction.

T. M. L.

**Origin of the Elements. Some Stereochemical Views on the Question of the Unity of Matter.** By PAUL HELLSTRÖM (*Zeit. anorg. Chem.*, 1901, 29, 95—106).—The author believes that the elements have been formed from a primordial matter, the differences between them being due to the different polyhedral forms into which it has aggregated. He explains valency as due to attractions in particular directions in the aggregated mass. The periodicity of the properties of the elements leads to the conclusion that one series occurs in each of

the seven holohedral forms of the regular crystallographic system. The elements of the eighth series have a form with varying parametral ratio.  
J. McC.

**The Periodic System of the Elements.** By H. STAIGMÜLLER (*Zeit. physikal. Chem.*, 1901, **39**, 245—248).—Another variation of the classification of the elements for which the author claims that the elements fall into more natural groups, and that the non-metals become separated from the metals.  
L. M. J.

**Third Report of the Committee [of the German Chemical Society] on Atomic Weights.** By the Members of the Committee: HANS LANDOLT, WILHELM OSTWALD, and KARL SEUBERT (*Ber.*, 1901, **34**, 4353—4384. Compare *Abstr.*, 1899, ii, 86; 1900, ii, 533).—Further inquiry has been made by the Committee in order to discover the views of chemists on the question whether the basis of atomic weights shall be taken as  $H=1$  or  $O=16\cdot00$ . Of the total number of answers received, 106 were in favour of  $H=1$  and 78 in favour of  $O=16\cdot00$ .

Since the last report, the Committee have recommended that the atomic weight of iron be changed from 56 to 55·9, and that of calcium from 40 to 40·1.  
K. J. P. O.

**Theory of Unsaturated Compounds.** By F. WILLY HINRICHSSEN (*Zeit. physikal. Chem.*, 1901, **39**, 304—310).—The assumption is made that atoms have an invariable affinity or saturation capacity, and reasons must be sought in order to explain why this does not reach its maximum in certain cases. Temperature is one cause, as van't Hoff (*Ansichten ueber organische Chemie*) has shown, and another cause is the electrochemical character of the components. Blomstrand (*Chemie der Jetztzeit*) points out that when a strongly positive or negative element acts with its full positive or negative force, it is always found in its lowest degree of saturation; thus, when the halogens form salts, that is, act decidedly negatively, they are always univalent. Blomstrand further points out that the energy content of an atom is the greater, the fewer affinity units come into play.

The author believes that all cases of unsaturated compounds are to be explained by assuming that the valency is constant, but part of the affinity, from one or both of the above causes, remains in abeyance.

Baeyer's tension theory, and Thiele's theory of partial valency, do not agree with the behaviour of many organic compounds, and there is now no reason to believe that carbon may not occur with free valencies, as in carbon monoxide ( $C\cdot O$ ), hydrocyanic acid ( $C\cdot NH$ ), isonitriles ( $C\cdot NR$ ), and fulminic acid ( $C\cdot N\cdot OH$ ).

The explosive nature of acetylene ( $C\cdot CH\cdot CH\cdot$ ) is explained by the great content of energy of the bivalent carbon which it contains, according to Blomstrand's hypothesis. The 1:4 rule for the formation of additive compounds can also be explained by the assumption of free valencies.  
J. McC.

**Simple Lecture Experiments to Demonstrate the Dissociation, on Heating, of the Chloride and other Salts of Ammonium.** By DIOSCORIDE VITALI (*L'Orosi*, 1901, **24**, 332—334).—The dissociation of ammonium chloride may be shown by heating it

in presence of a small quantity of a mixture of potassium iodide and iodate ; the hydrogen chloride evolved acts on these two salts, forming hydriodic and iodic acids, which react to yield iodine, the latter then volatilising as a violet vapour. The ammonia also formed in this reaction may be detected, not only by its odour, but also by its action on turmeric paper and by the white fumes formed in presence of a rod moistened with hydrochloric acid. Also, in solution, iodine is obtained by heating ammonium chloride or sulphate in presence of potassium iodide and iodate. Instead of the iodine salts, a mixture of potassium bromide and bromate, or of chloride and chlorate, may be employed.

T. H. P.

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## Inorganic Chemistry.

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**Reaction between Nitric Acid and Hydrogen Iodide.** By ADOLF ECKSTÄDT (*Zeit. anorg. Chem.*, 1901, 29, 51—94).—So long as air is free from dust, it has no influence on the action between nitric and hydriodic acids. Scratches on the flask in which the reaction takes place accelerate the reaction to an enormous extent. The order of the reaction between nitrous acid and hydriodic acid could not be determined; the reaction takes place very rapidly at first, but soon slackens. Reaction takes place directly ( $\text{NO}_3' + 2\text{H}\cdot + 2\text{I}' = \text{NO}_2' + \text{H}_2\text{O} + \text{I}_2$ ) between nitric acid and hydriodic acid, for when carbamide is added in order to destroy any nitrous acid present, the action has a normal course. Hydrogen ions exert a catalytical influence on the reaction.

Ferric ions, as well as sixteen other cations examined, have no catalytic influence whatever on the reaction. Ferrous ions enormously accelerate the reaction, the influence being independent of the anion present.

It was observed that when about two-thirds of the hydriodic acid had been decomposed, a great acceleration took place, so that the reaction thereafter quickly completed itself, and this is attributed to the influence of the iodine produced. Tri-iodine ions can only be formed so long as iodine ions are present, that is, until about two-thirds of the hydriodic acid is used up. Then the action of the oxidiser ceases, or iodine is separated in the colloidal state or as a solid, and this, giving rise to new iodine ions, restarts the reaction, which proceeds until it is complete.

When the reaction takes place in an electric field, no difference in the rate could be detected. J. MCC.

**Spontaneous Decomposition of Ozone.** By EMIL WARBURG (*Sitzungsber. K. Acad. Wiss. Berlin*, 1901, 48, 1126—1139).—The spontaneous decomposition of ozone, where external causes of decomposition are excluded, is a bimolecular reaction. At the ordinary temperature, the results obtained indicate that the decomposition takes place in



accordance with the formula for a monomolecular reaction, but this is attributed to the disturbing influence of the glass walls of the containing vessel. The influence of external agents on the speed of decomposition increases much more slowly with rising temperature than does the actual velocity of the bimolecular reaction. The quantity,  $b$ , of ozone which is decomposed per minute can be ascertained from  $dC = -bC^2dt$ , where  $C$  is the number of gram-mols. of ozone per litre and  $t$  is the time. The value of  $b$  at  $100^\circ$  is  $0.0157$ , and at  $126.9^\circ$  it is  $0.177$ . The velocity quotient for  $10^\circ$  is  $2.47$ . Shenstone (*Trans.*, 1897, 71, 477) states that at  $26^\circ$  moist ozone is more stable than dry; the author finds that, at  $100^\circ$ , the dry gas is just as stable as the moist.

J. McC.

**Sublimed Sulphur.** By NORMAN LEONARD (*Analyst*, 1901, 26, 319—320).—Although sublimed sulphur B.P. is not supposed to affect blue litmus, the author has found it generally to contain from 0.02 to 0.25 per cent. of sulphuric acid. Although part of the acid may be formed during the process of sublimation, it is also formed by exposure to air and moisture. A sample of sublimed sulphur, after being washed until no longer acid, was put in a moist condition into a stoppered bottle; after two weeks, it was found to be faintly acid, and decidedly so after three months, whilst after four years it contained 0.2 per cent. of sulphuric acid; sulphurous acid could not be detected. A specimen which had been washed, and dried at  $100^\circ$ , only showed 0.0025 per cent. of acid after having been kept for four years.

L. DE K.

**Viscosity of Sulphur.** By CH. MALUS (*Ann. Chim. Phys.*, 1901, 24, [vii], 491—574).—Sulphur, when heated for 5—10 minutes at  $357^\circ$ , is black and on cooling to  $100^\circ$  becomes pale yellow. The modification of the element produced in this way is indicated by the symbol  $S_1$ ; it is viscous at  $100^\circ$  and contains bubbles of sulphur dioxide; at  $15^\circ$ , it becomes plastic (compare *Abstr.*, 1900, ii, 536). Another modification,  $S_2$ , is produced when the heating at  $357^\circ$  is prolonged for 3 hours; this form is lighter in colour than  $S_1$ , being almost colourless at  $73^\circ$ ; it is not viscous at  $100^\circ$ , and contains no gaseous bubbles at this temperature, and at the ordinary temperature it becomes quite hard. Sulphur heated at  $300^\circ$ , or at higher temperatures, passes ultimately into the modification  $S_2$ , the rate of change depending on the temperature; complete transformation requires 30 hours at  $300^\circ$  but only 15 minutes at  $440^\circ$ . The modification  $S_1$  owes its existence to the presence of sulphur dioxide in the sulphur and its conversion into  $S_2$  is due to the expulsion of the gas; any causes which tend to eliminate the gas more rapidly, such as the introduction of thin glass rods or the passage of carbon dioxide, increase the velocity of transformation. Moreover,  $S_2$  is reconverted into  $S_1$  when heated at  $357^\circ$  in the presence of sulphur dioxide. On the other hand, the variety  $S_1$  does not change into  $S_2$  on prolonged heating at this temperature if it is kept saturated with sulphur dioxide.

Sulphur in form of  $S_1$  is slowly converted into a third modification  $S_2'$  when maintained in superfused condition at temperatures varying from  $72^\circ$  to  $103^\circ$ ; this third variety differs from  $S_2$  in becoming viscous when heated at  $180^\circ$  or at higher temperatures. This difference is

due to the fact that, in the transformation of  $S_1$  into  $S_2'$ , there is no elimination of sulphur dioxide and therefore the latter modification still contains the dissolved gas which at higher temperatures promotes the formation of the  $S_1$  variety. G. T. M.

**Determination of the Vapour Density of Sulphur by the Dumas Method.** By HEINRICH BILTZ and GERHARD PREUNER (*Zeit. physikal. Chem.*, 1901, **39**, 323—341).—A full account of the apparatus used in determining the vapour density of sulphur at  $448^\circ$  under varying pressures. The conclusions are to be found in Abstr., 1901, ii, 649. As the quaternary reaction  $S_8 \rightleftharpoons 4S_2$  is improbable, the authors believe that the dissociation may take place in the two stages:  $S_8 \rightleftharpoons 2S_4$  and  $S_4 \rightleftharpoons 2S_2$ . J. McC.

**Apparatus for Experimenting with Sulphur Trioxide.** By HERMANN WICHELHAUS (*Ber.*, 1901, **34**, 4135).—A test-tube widened at the open end fits concentrically into a cylindrical glass receiver into which sulphur trioxide is distilled. The test-tube is filled with fragments of ice and the trioxide condenses on its cooled outer surface. When sufficient of the compound has been collected, the tube is withdrawn and another placed in position. In this way, samples of sulphur trioxide available for lecture experiments are readily obtained. G. T. M.

**Sulphuric Acid and its Manufacture by the Contact Process.** By RUDOLF KNIETSCH (*Ber.*, 1901, **34**, 4069—4115).—An account of the historical development and recent introduction on a large scale of the contact process of making sulphuric acid.

When the gases obtained by roasting pyrites are freed from mechanical impurities, and passed in a dry state through tubes containing a catalytic agent (for example, platinised asbestos), a practically quantitative yield of sulphur trioxide can be obtained at first, but the activity of the contact substance, and, consequently, the yield of sulphur trioxide, gradually diminish. It is found that certain substances, notably arsenic, mercury, and phosphorus, have a remarkably deleterious effect on the catalytic action of platinum, and the above-mentioned deterioration of the contact substance is due to the presence of arsenic in the pyrites gases. It is exceedingly difficult to get rid of the last traces of arsenic. Thus troublesome fogs of finely divided unburnt sulphur particles, containing arsenic and almost unprecipitable, are produced in the pyrites ovens, and the only remedy is to blow in steam, thus securing thorough mixture of the pyrites gases and complete combustion of the sulphur. Finally, by cooling and washing the gases in a very thorough manner, it has been found possible to free them from all hurtful impurities, and to preserve the contact substance in excellent condition.

The tubes containing the contact substance should be heated previous to the passing of the pyrites gases, but, the process having been started, very little external heat is necessary, since the heat of the reaction,  $2SO_2 + O_2 = 2SO_3$ , is very considerable, and the temperature must not be allowed to rise too high. In the apparatus described in

the paper, it was found necessary actually to cool the tubes by a current of cold air in order to procure the best results. In this contact process, the gases are not under pressure: indeed, the yield is not appreciably affected by diluting the pyrites gases largely with air.

The sulphur trioxide produced can be instantaneously and completely absorbed by sulphuric acid of 97—99 per cent., a behaviour shown by sulphuric acid of no other concentration. Acid of this "critical" concentration is peculiar in other respects also, as the author shows by a study of the boiling point curve, the sp. gr., the electrical resistance, and the action on cast and wrought iron. The gas issuing from the contact tubes can be completely freed from sulphur trioxide in a single apparatus, provided the acid in this apparatus is kept of the proper strength by regular addition of water or dilute acid, and removal of the excess of acid formed by the absorption.

The contact process does not give a quantitative yield when the sulphur dioxide and oxygen are mixed in the proportion required by the equation:  $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ ; the more oxygen there is in proportion to the sulphur dioxide, the more productive is the process; nitrogen is without effect on the reaction. When the pyrites gases, which contain sulphur dioxide and oxygen approximately in the ratio  $2\text{SO}_2 : 3\text{O}_2$  and in addition 83 per cent. of nitrogen, are passed over platinised asbestos in a porcelain tube, and the temperature of the tube is varied, it is found that at 400—430° 98—99 per cent. of the sulphur dioxide is converted into sulphur trioxide, whilst further rise of temperature has a bad effect on the yield; thus, at 700—750°, the yield is only 60 per cent., and at 900—1000° there is practically no reaction at all between sulphur dioxide and oxygen. In the absence of contact substance, however, sulphur trioxide is stable even at high temperatures. The formation of trioxide from dioxide and oxygen depends, too, on the rate at which the gases are passed over the contact substance, and for each temperature there is a certain rate which gives the maximum yield. Platinum alone fulfils the conditions necessary for an effective contact substance.

The paper contains also a detailed study of the physical properties of mixtures of water and sulphur trioxide in varying proportions. The melting point curve shows maxima for mixtures of the composition  $2\text{H}_2\text{O} + \text{SO}_3$ ,  $\text{H}_2\text{O} + \text{SO}_3$ ,  $\text{H}_2\text{O} + 2\text{SO}_3$ , the melting points of these three being respectively 8°, 10°, and 36°. When density is plotted against percentage composition, the resulting curve shows two maxima, one at 79.72 per cent.  $\text{SO}_3$  (= 97.66 per cent.  $\text{H}_2\text{SO}_4$ ) and the other at 92.65 per cent.  $\text{SO}_3$ , the corresponding densities being 1.8434 and 2.020 at 15°; the density of sulphur trioxide is 1.984 at 15° and 1.814 at 45°. The specific heat falls with increasing percentage of the trioxide to the value 0.339 for an acid containing about 20 per cent. of the free anhydride; the specific heat of absolute sulphur trioxide is 0.770. The heat of solution varies in a perfectly continuous manner with the percentage, and it therefore appears that the formation of the various hydrates is not accompanied by any appreciable heat effect. The observations made on the electrical resistance agree with those of Kohlrausch (*Ann. Phys. Chem.*, 1882, [ii], 17, 69), except that the

author finds a maximum value of the resistance at 99.9—99.95 per cent.  $\text{H}_2\text{SO}_4$  instead of at 99.74—99.75. With acids containing more trioxide, there is first a fall of resistance, and finally a steady increase to very high values. The boiling point curve shows a maximum, and the vapour pressure curve a minimum for the composition 80.4 per cent.  $\text{SO}_3$  (= 98.5 per cent.  $\text{H}_2\text{SO}_4$ ). By allowing equal volumes of acid of varying concentration to flow through a narrow opening, it is found that water and absolute sulphur trioxide have approximately the same viscosity; the maximum viscosity corresponds with the point of maximum density for the fuming acid. The height reached in a capillary tube gradually diminishes with increasing percentage of trioxide, although there are slight peculiarities in the curve at the hydrate  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ , and at the point of maximum density. Finally, a table is appended for converting the percentages of total  $\text{SO}_3$ , found by analysis of the fuming acid, into percentages of free  $\text{SO}_3$ .

J. C. P.

**Allotropy of Tellurium.** By DMITRI BELJANKIN (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 670—676).—The variation in the values given for the specific heats of amorphous tellurium is explained by the author as due to the fact that the modification obtained by Berthelot by precipitation from alkaline solution and described by him as amorphous, consists in reality of microscopic rhombohedra. For the densities of various modifications of tellurium at 18—22°, the author obtains the following numbers: (1) Amorphous tellurium (precipitated from acid solution by means of sulphur dioxide),  $6.015 \pm 0.031$ . (2) Ordinary crystalline tellurium,  $6.338 \pm 0.025$ . (3) Berthelot's crystalline tellurium (obtained from alkaline solution),  $6.157 \pm 0.035$ . By slowly heating to 430°, the density of (2) is unchanged, but (1) increases and (3) decreases in density; these alterations point to the existence of a third crystalline form of tellurium, which has not, however, been isolated.

Other unknown modifications are also indicated by results obtained by Berthelot (Abstr., 1887, 761) and by Töpler (Abstr., 1895, ii, 5).

T. H. P.

**Telluric Acid.** By ALEXANDER GUTBIER (*Zeit. anorg. Chem.*, 1901, 29, 22—35. Compare Abstr., 1901, ii, 501).—Telluric acid has been prepared by the method devised by Staudenmaier. No evidence could be found of the existence of an acid of the formula  $\text{H}_2\text{TeO}_4$ . The acid when heated at 145° loses water and at the same time oxygen, and in the residue both the oxides  $\text{TeO}_3$  and  $\text{TeO}_2$  are to be found. Telluric acid is dimorphous, crystallising in regular and hexagonal-rhombohedral forms, the latter being the more common.

The determination of the molecular conductivity shows that the acid is only very slightly dissociated and this is confirmed by the depression of the freezing point of water. The equivalent conductivity of the normal potassium salt differs greatly from that of potassium sulphate, but agrees well with that of potassium carbonate.

The formula of telluric acid is, as previously stated (*loc. cit.*),  $\text{H}_6\text{TeO}_6$ , and not  $\text{H}_2\text{TeO}_4 + 2\text{H}_2\text{O}$ .

J. McC.

**Some Physical Properties of Nitric Acid Solutions.** By VICTOR H. VELEY and J. J. MANLEY (*Proc. Roy. Soc.*, 1901, **69**, 86—119).—Details are given of work already reviewed (*Abstr.*, 1901, ii, 447), dealing with the densities and refractive indices of nitric acid solutions. The maximum refractive index observed (1.4061 at 14.2°) is that of a solution containing 70 per cent. of nitric acid; the refractive index of the anhydrous acid is nearly the same as that of a solution containing equal parts by weight of acid and water. The possible errors involved in the various physical measurements are discussed and estimated. J. C. P.

**Action of Hydrogen Sulphide on Arsenic Acid.** By LE ROY W. McCAY (*Zeit. anorg. Chem.*, 1901, **29**, 36—50. Compare *Abstr.*, 1889, 15; 1898, ii, 139; 1899, ii, 745).—Monothioxyarsenic acid is formed when hydrogen sulphide acts on arsenic acid solution ( $\text{H}_3\text{AsO}_4 + \text{H}_2\text{S} = \text{H}_3\text{AsO}_3\text{S} + \text{H}_2\text{O}$ ). Dithioxyarsenic acid is also obtained but is not a direct product of the reaction; it is probably formed from the monothioxyarsenic acid ( $\text{H}_3\text{AsO}_3\text{S} + \text{H}_2\text{S} = \text{H}_3\text{AsO}_2\text{S}_2 + \text{H}_2\text{O}$ ).

Magnesium oxide is a good reagent for the separation of arsenic acid from monothioxyarsenic acid, for whilst the magnesium arsenate is insoluble, magnesium monothioxyarsenate is easily soluble. *Sodium monothioxyarsenate*,  $\text{Na}_3\text{AsO}_3\text{S} \cdot 12\text{H}_2\text{O}$ , has been obtained in the pure condition from arsenic acid by passing hydrogen sulphide through a solution of it, filtering, and then leaving the filtrate for 24 hours in contact with excess of magnesium oxide; to the filtrate from the magnesium precipitate, alkali is added in quantity sufficient to precipitate all the magnesium; on adding barium hydroxide to the filtered solution, a precipitate of sodium barium monothioxyarsenate is formed, which is exactly decomposed with sodium carbonate or sulphate and the sodium monothioxyarsenate thrown down in crystals by the addition of alcohol.

*Sodium dithioxyarsenate*,  $\text{Na}_3\text{AsO}_2\text{S}_2 \cdot 11\text{H}_2\text{O}$ , is prepared by allowing an excess of hydrogen sulphide to act on a solution of arsenic acid for some time, then expelling the excess of gas, and treating the solution with strontium hydroxide; the arsenic and monothioxyarsenic acids are then removed and barium hydroxide added to the filtrate to precipitate barium dithioxyarsenate, which is converted into the sodium salt by treatment with sodium sulphate. J. McC.

**Condition of Silicon in Cast Iron and Ferrosilicon.** By PAUL LEBEAU (*Compt. rend.*, 1901, **133**, 1008—1010).—Nitric acid and cupric potassium chloride have no action on very finely divided amorphous silicon, and hence the fact that these reagents dissolve or oxidise the silicon in cast iron and ferrosilicons containing a low proportion of silicon shows that in these substances the silicon must be in the form of iron silicides. The author has obtained only three definite compounds of iron and silicon,  $\text{Si}_2\text{Fe}$ ,  $\text{SiFe}$ , and  $\text{SiFe}_2$ . The first is found only in presence of excess of silicon and therefore cannot exist in cast iron and similar products. The monosilicide is readily dissociated and cannot exist in a matrix poor in silicon; it is decom-

posed into silicon and the compound  $\text{SiFe}_2$  when fused with silver. The silicide,  $\text{SiFe}_2$ , which contains the lowest proportion of silicon of any compound of the two elements which the author was able to obtain, is stable even at  $1000^\circ$ ; it dissolves in melted silver but is not decomposed. This is the form in which silicon exists in siliceous cast iron and its uniform distribution is due to the ease with which it dissolves in iron, whilst the consequent fine state of division in which it exists in the solidified metal is the reason why it is gradually attacked by nitric acid, which is almost without action on this silicide if it has been produced in the electric furnace.

C. H. B.

**Radium.** By MARCELLIN BERTHELOT (*Compt. rend.*, 1901, 133, 973—975).—The decomposition of iodic acid by radium (this vol., ii, 18) is due to the phosphorescent rays and does not take place either at  $10^\circ$  or  $100^\circ$  if a screen of black paper is placed between the radium and the iodic acid. The action of radium on glass is more rapid at  $100^\circ$  than at the ordinary temperature.

C. H. B.

**Preparation and Properties of Potassium Hydride.** By HENRI MOISSAN (*Compt. rend.*, 1902, 134, 18—21).—The action of hydrogen on potassium at  $360^\circ$  yields the hydride,  $\text{KH}$ , in slender, white, acicular crystals, very readily decomposed by atmospheric moisture and by water. It takes fire at the ordinary temperature in fluorine, chlorine, or oxygen, and when gently heated decomposes carbon dioxide, hydrogen sulphide, and lead and copper oxides. It does not react with liquid ammonia under the ordinary pressure, but in sealed tubes a compound is formed which dissolves in excess of the liquid; when heated in ammonia gas at about  $400^\circ$ , potassamide is formed. Potassium hydride is insoluble in terebenthene, benzene, ether, or carbon disulphide.

C. H. B.

**Melting Points of Alloys of Sodium with Potassium.** By NICOLAI S. KURNAKOFF and N. A. PUSHIN (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 588—592).—The relations between melting point and composition are given, in the form of curves and tables, for mixtures of sodium and potassium. The melting point curve shows a transition point ( $6.88^\circ$ ) for the alloy of the composition  $\text{Na}_{1.497}\text{K}$  and a eutectic point,  $-12.5^\circ$ , corresponding with the compound  $\text{NaK}_2$ .

T. H. P.

**Rubidium and Cæsium Phosphates.** By EDUARD VON BERG (*Ber.*, 1901, 34, 4181—4185).—*Rubidium dihydrogen phosphate*,  $\text{RbH}_2\text{PO}_4$ , obtained by evaporating an aqueous solution containing mol. proportions of rubidium hydroxide and phosphoric acid, crystallises in large, colourless, anhydrous prisms and is acid to litmus. *Dirubidium hydrogen phosphate*,  $\text{Rb}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$ , is obtained by concentrating an aqueous solution of the proper quantities of phosphoric acid and rubidium carbonate, adding ammonia to precipitate a crystalline *rubidium ammonium phosphate*, and drying the latter in a vacuum over sulphuric acid until all the ammonia is removed; if the treatment with ammonia is not adopted, the salt cannot be obtained

crystalline; its solution is alkaline to litmus. *Trirubidium phosphate*,  $\text{Rb}_3\text{PO}_4 \cdot 4\text{H}_2\text{O}$ , obtained by concentrating an aqueous solution of phosphoric acid (2 mols.) and rubidium carbonate (3 mols.), crystallises in short, thick, colourless, hygroscopic prisms. *Rubidium metaphosphate*,  $\text{RbPO}_3$ , obtained by heating the monorubidium phosphate, is a white powder, which, unlike the analogous sodium and potassium salts, is soluble in water. *Rubidium pyrophosphate*,  $\text{Rb}_4\text{P}_2\text{O}_7$ , is a white, hygroscopic mass.

*Cæsium dihydrogen phosphate*,  $\text{CsH}_2\text{PO}_4$ , forms beautiful, colourless, lustrous, anhydrous plates; *dicæsium hydrogen phosphate*,  $\text{Cs}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$ , which is very soluble in water, is a white, microcrystalline solid, whilst *tricæsium phosphate*,  $\text{Cs}_3\text{PO}_4 \cdot 5\text{H}_2\text{O}$ , forms small, white, deliquescent crystals with an alkaline reaction. *Cæsium metaphosphate* and *pyrophosphate* are similar to the analogous rubidium compounds.

W. A. D.

**Combining Weight of Calcium.** By F. WILLY HINRICHSSEN (*Zeit. physikal. Chem.*, 1901, 39, 311—322).—The weight of calcium oxide left on ignition of about 30 grams of Iceland spar in an electric furnace of suitable form was determined. The Iceland spar gave 0.032 per cent. of ferric oxide and contained neither silicic acid nor magnesium, and only a trace of aluminium. During the ignition, the spar was heated in a platinum crucible furnished with a lid through which two tubes passed. A current of purified air was drawn through the apparatus during the experiment, and the tubes were carefully closed during weighing to prevent access of moisture and carbon dioxide. Four experiments gave a mean value of 40.142 for the atomic weight of calcium when  $\text{O} = 16$ .

J. McC.

**Formation of Oceanic Salt Deposits, particularly of the Stassfurt Beds. XXIV. Gypsum and Anhydrite. 3. Natural Anhydrite and its Formation at 25°.** By JACOBUS H. VAN'T HOFF and FRITZ WEIGERT (*Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 48, 1140—1148. Compare Abstr., 1901, ii, 506, and this vol., ii, 74).—In presence of sodium chloride, the transition point of gypsum is lowered; by dilatometric experiments, it has been found that the transition in this case takes place near 30°. The tension of the gypsum-anhydrite mixture at this temperature is the same as that of the saturated sodium chloride solution and has been found to be 24 mm.

In presence of sodium bromate, the transition takes place near 50°, and the tension is then 83.3 mm. The tension at any other temperature can be found from the formula  $\log P_g = \log P_w - 341/T + 1.0072$ , where  $P_g$  is the tension of the gypsum and  $P_w$  that of water at the temperature  $T$ .

In concluding the work on the transition of gypsum, the authors sum up the results obtained as follows. Gypsum is transformed (1) into natural anhydrite:

A. At 66°. B. In presence of sodium chloride at 30°.

(2) Into soluble anhydrite:

C. At 89°. D. In presence of sodium chloride at 65°.

(3) Into semihydrate:

E. At 107°. F. At 101.5°, under atmospheric pressure (boiling

point) G. In presence of magnesium chloride at  $11^{\circ}$ . H. In presence of sodium chloride at  $76^{\circ}$ .

Solutions containing calcium sulphate which have a tension lower than 17.2 mm. at  $25^{\circ}$  deposit it as anhydrite. This is the case in the deposition from sea-water. J. McC.

**Metallic Strontium and its Hydride.** By ANTOINE GUNTZ (*Compt. rend.*, 1901, 133, 1209—1210. Compare Gautier, following abstract).—Strontium amalgam is very easily prepared when an aqueous solution of strontium chloride is electrolysed, using mercury as cathode. From the amalgam, metallic strontium is obtained by distilling off the mercury in a vacuum. *Strontium hydride*,  $\text{SrH}_2$ , is prepared by heating strontium or its amalgam in a current of hydrogen, and is a white solid which fuses only at a red heat. Strontium does not dissolve in liquid ammonia as does barium. K. J. P. O.

**Alloys of Strontium with Zinc and Cadmium.** By HENRI GAUTIER (*Compt. rend.*, 1901, 133, 1005—1008).—An alloy of zinc and strontium containing 12—14 per cent. of the latter can be obtained by the action of sodium on a mixture of strontium and zinc chlorides, the excess of sodium being removed by treatment with alcohol. A similar alloy containing 18 per cent. of strontium is obtained by the action of sodium on strontium iodide in presence of zinc. Attempts to obtain richer alloys by partially volatilising the zinc were unsuccessful, since both metals volatilised together. Cadmium strontium alloys containing 18 to 20 per cent. of strontium were obtained in a similar manner, and by heating these at  $250\text{--}300^{\circ}$  in a vacuum the strontium is concentrated up to as much as 45 per cent. The latter alloy can be polished with a file, but the surface rapidly tarnishes; it burns readily in oxygen, phosphorus vapour, and chlorine, and reacts with sulphur below its boiling point and with iodine at a dull red heat. When heated at dull redness in hydrogen, a white strontium hydride,  $\text{SrH}_2$ , is formed and can be isolated by volatilising the cadmium in a vacuum. C. H. B.

**Preparation of Barium.** By ANTOINE GUNTZ (*Compt. rend.*, 1901, 133, 872—874).—Barium amalgam, which is readily obtained by electrolysing a concentrated solution of barium chloride in contact with a mercury cathode, is heated in a porcelain tube by means of an electric current passed through a thin platinum wire until a temperature of  $1150^{\circ}$  is reached. All the mercury is driven off at lower temperatures, and the final distillate consists of barium containing 97.8 per cent. of the metal. This element, when freshly cut, has a silvery lustre, but it rapidly oxidises and often takes fire in the atmosphere. The metal melts below  $1000^{\circ}$ , and is readily volatilised at a bright red heat; it yields, with liquid ammonia, a compound which seems to be more stable than its lithium and calcium analogues.

Barium readily decomposes water, absolute alcohol, and even a solution of barium ethoxide. G. T. M.

**Preparation of Barium.** By EDGAR STANSFIELD (*Mem. Manchester Phil. Soc.*, 1901, 46, No. 4, 1—6).—A solid, crystalline amal-



gam, containing nearly 5 per cent. of barium, can be easily obtained by the electrolysis of a saturated solution of barium chloride, using a mercury cathode. An alloy containing 12 per cent. of barium is obtained by heating a mixture of zinc, sodium, barium chloride, and sodium chloride. But in neither case can pure barium be obtained by distillation of the mercury or zinc. A hard, thick, metallic mass containing crystalline flakes and nodules of metal is obtained by heating barium peroxide with finely divided aluminium in a vacuum. It contains 63.3 to 66.6 per cent. of barium, and 19.3 to 29.3 per cent. of aluminium; the metallic nodules mentioned above contain 58 per cent. of barium and 42 per cent. of aluminium. The metallic flakes and nodules decompose water very rapidly but are stable when exposed to dry air. The results indicate that the reaction between barium peroxide and aluminium is a reversible one and that it cannot be used to obtain pure barium. With calcium oxide, the reaction did not take place, and on replacing the aluminium by magnesium, the reaction was too violent and shattered the apparatus. E. C. R.

**Action of Ammonia and Potassium Hydroxide on Solutions of Zinc Salts.** By BASIL B. KURILOFF (*Chem. Centr.*, 1901, ii, 1222; from *Bull. Acad. St. Petersb.*, 1901, No. 1, 95—103).—The excess of ammonia or potassium hydroxide which is necessary to dissolve the precipitate formed when the alkali is added to a solution of zinc chloride or sulphate has been determined, and the results show that in both cases the more dilute the solutions of ammonia or potassium hydroxide, the greater must be the actual proportion of alkali to zinc salt. Solutions weaker than decinormal do not appreciably affect the precipitate. The proportion of alkali required is also greater for solutions of the sulphate than for those of the chloride, but the data obtained for these two solutions are otherwise very similar. No quantitative determinations to show the influence of the chlorine or sulphate ions are given, but the solid phase which is formed when potassium hydroxide acts on zinc sulphate contains sulphate, and this group cannot be removed by washing with water. E. W. W.

**Alloys of Thallium.** By NICOLAI S. KURNAKOFF and N. A. PUSHIN (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 565—588).—The authors have determined the relations between melting point and composition for mixtures of thallium with the following metals: sodium, potassium, tin, cadmium, and mercury, the results being expressed both in curves and in tables. It is found that in combination with potassium or sodium, and also with tin or cadmium, thallium behaves similarly to heavy metals having an acid character, such as mercury and lead, which it also resembles physically in the free state; in alloys with mercury, bismuth, or lead, however, thallium plays a part similar to that of the alkali metals. The melting point curves for sodium-thallium, and potassium-thallium show eutectic points corresponding with alloys of the composition NaTl and KTl; the first of these compounds melts at 305.8° and the latter at 335.0°. The authors' results serve to complete the following series of sodium alloys: NaHg<sub>2</sub>, NaTl, Na<sub>2</sub>Pb, Na<sub>3</sub>Bi, in which it will be seen that corresponding with the

increase of the atomic weight and acid properties of the heavy metal, an increase occurs in the relative number of sodium atoms in a molecule of the alloy.

T. H. P.

**Action of Cupric Hydroxide on Aqueous Solutions of Metallic Salts.** By AMABLE MAILHE (*Compt. rend.*, 1902, 134, 42—45).—The action of the black hydrate of cupric oxide on aqueous solutions of various metallic sulphates yields the following results: with cadmium, at the ordinary temperature, bluish-green, rhombic plates of the compound  $2\text{CdSO}_4 \cdot 3\text{CuO} \cdot 12\text{H}_2\text{O}$ , and at  $100^\circ$ , green, hexagonal crystals of the compound  $2\text{CdSO}_4 \cdot 3\text{CuO} \cdot 10\text{H}_2\text{O}$ ; with nickel, strictly analogous compounds, in green crystals; with cobalt, at the ordinary temperature, maroon coloured crystals of the compound  $3\text{CoSO}_4 \cdot 5\text{CuO} \cdot 16\text{H}_2\text{O}$ , and at  $100^\circ$ , maroon coloured, hexagonal plates of the compound  $2\text{CoSO}_4 \cdot 3\text{CuO} \cdot 10\text{H}_2\text{O}$ . With zinc at the ordinary temperature, the composition of the product varies with the concentration of the solution from  $\text{ZnSO}_4 \cdot 3\text{CuO} \cdot 5\text{H}_2\text{O}$  to  $2\text{ZnSO}_4 \cdot 3\text{CuO} \cdot 12\text{H}_2\text{O}$ , the latter being the sole product at  $100^\circ$ . Manganese is not displaced from manganous sulphate by cupric oxide, but mercury, aluminium, and iron (ferric) are completely displaced (compare Abstr., 1901, ii, 601).

C. H. B.

**The Oxidising Action of Copper Salts.** By EDUARD SCHAEER (*Arch. Pharm.*, 1901, 239, 610—626. Compare Abstr., 1900, i, 512; ii, 583).—An account of the way in which different substances accelerate the oxidising action of cupric salts, especially its salts with the organic acids, on iodide of starch, guaiacum, indigo, cyanine, pyrogallol, brazilin, aniline, *p*-phenylenediamine, guaiacol, or aloin. Hydrocyanic acid, soluble ferrocyanides, ferricyanides, thiocyanates, and nitroprussides, cyanogen iodide, organic cyanides and thiocarbimides, iodine, bromides and chlorides, ammonia and alkaloids, hydrogen peroxide, sulphurous acid and sulphites, and colloidal platinum and gold are all found to produce a greater or less acceleration.

C. F. B.

**Praseodymium Peroxide and Dioxide.** By PETR. G. MELIKOFF and B. E. KLIMENKO (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 663—666).—The basic character of the two oxides of praseodymium, observed by former investigators, indicates that this element cannot be placed in the periodic system between niobium and tantalum.

On cautiously adding dilute potassium hydroxide solution to a hydrogen peroxide solution of the sulphate or nitrate of the metal, a pale green, gelatinous precipitate is formed, having in the first instance the probable formula  $\text{Pr}(\text{O}_2\text{H})_3$ ; this compound, however, quickly decomposes, yielding free oxygen and the hydrate of praseodymium monoperoxide,  $\text{Pr}(\text{OH})_2 \cdot \text{O}_2\text{H}$ , which loses water when kept. Under the action of dilute sulphuric acid, this hydrated peroxide yields hydrogen peroxide, whilst with the concentrated acid ozone is formed; aqueous potassium hydroxide is oxidised by the hydrate to potassium peroxide, but no conversion of manganese salts into permanganic acid takes place in presence of nitric acid.

Praseodymium dioxide,  $\text{PrO}_2$ , yields, with dilute sulphuric acid, no

hydrogen peroxide but ozone ; in presence of nitric acid, however, it oxidises manganese sulphate to permanganic acid.

The author concludes that the peroxide  $\text{Pr}_2\text{O}_5$  is a compound of the type  $\text{H}_2\text{O}_2$ , but that the dioxide cannot be regarded as such.

T. H. P.

**Alloys of Aluminium and Magnesium.** By OCTAVE BOUDOUARD (*Compt. rend.*, 1901, 133, 1003—1005).—By treating fused mixtures of aluminium and magnesium in various proportions with ammonium chloride solution or dilute hydrochloric acid, the author has isolated three definite crystalline compounds of the two metals:  $\text{AlMg}_2$ , sp. gr. 2.03, from a mixture of 30 parts of aluminium and 70 parts of magnesium;  $\text{AlMg}$ , sp. gr. 2.15, from mixtures of 40 to 50 parts of aluminium with 60 to 50 parts of magnesium, and  $\text{Al}_4\text{Mg}$ , sp. gr. 2.58, from mixtures of 70 parts of aluminium and 30 parts of magnesium. All the fused mixtures of the two metals, except that containing equal parts of each, show dendritic crystals in considerable quantity. The existence of the compounds  $\text{AlMg}_2$  and  $\text{AlMg}$  was predicted from determinations of the melting points of the two metals (Abstr., 1901, ii, 512).

C. H. B.

**Action of Aluminium on Salt Solutions and on Molten Salts.** By CARLO FORMENTI and MARIO LEVI (*Chem. Centr.*, 1901, ii, 1298; from *Boll. Chim. Farm.*, 1901, 40, 689—696).—From experiments on the reduction of salts of gold, platinum, palladium, cadmium, lead, tin, beryllium, cerium, niobium, thorium, zirconium, chromium, uranium, thallium, ammonium, zinc, iron, manganese, mercury, antimony, arsenic, bismuth, silver, copper, cobalt, nickel, silicon, and boron by aluminium, this metal is found to be a more powerful reducing agent than the metals commonly used for this purpose. In many cases, the aluminium does not completely replace the metal which is contained in the salt, and the reduced metal is often mixed with more or less aluminium, forming an alloy. In other cases, the metal which first separates subsequently forms a basic salt or is oxidised. By the action of aluminium on some sulphates, alums are formed, and the metal even attacks aqueous solutions of aluminium chloride, forming a hydrate of a subchloride and liberating hydrogen. The reduction of metallic chlorides takes place the more readily the greater the difference between the heat of formation of aluminium chloride and that of the metallic chloride, and this is also the case with other salts.

E. W. W.

**Preparation of Crystallised Alumina in the Electric Furnace and some By-products of this Process.** By WILHELM H. GINTL (*Zeit. angew. Chem.*, 1901, 14, 1173—1179).—Different specimens of bauxite, with a small amount of powdered coal and a quantity of sodium chloride, were fused in an electric furnace. A 100 volt current was used. After the whole mass had become fused, it was allowed to run out; at first, a limpid metal flowed out, and was followed by a more viscid slag. The metal is brittle, and its density (at  $15^\circ$ ) varies between 6.75 and 6.78. It consists chiefly of iron (83

per cent.) and silicon (14 per cent.), and small amounts of manganese, aluminium, carbon, phosphorus and titanium. The slag, on cooling, assumes a microcrystalline structure and is of a grey or brownish-grey colour. On breaking up the slag, small quantities of another metal and large blue and brown crystals were obtained; the metal consists mainly of aluminium (61 per cent.), iron (13 per cent.), and silicon (19 per cent.), along with smaller quantities of carbon, titanium, sodium, calcium, copper, and sulphur.

The blue and brown crystals were examined crystallographically; they have the same form, and belong to the hexagonal-rhombohedral system ( $0001:10\bar{1}1 = 57^{\circ}33'$ , which is nearly identical with the corresponding angle on natural corundum), and are uniaxial. The brown crystals (sp. gr. 3.55) contain about 82 per cent. of alumina, about 12.25 per cent. of silica, and small quantities of iron, manganese, sodium, and titanium. The blue crystals (sp. gr. 3.81) contain from 66 to 70 per cent. of alumina, about 16 per cent. of silica, considerable quantities of the oxides of iron and sodium, and smaller amounts of manganese, calcium, magnesium, and titanium oxides.

The author believes that the blue colour is due to the presence of a low oxide of titanium, and not to cobalt, because the presence of the former element has been established, but no cobalt could be detected, even when large quantities of the crystals were used. The titanium oxide is reduced by the carbon electrode at the high temperature. It was found that when pure alumina was fused with alkali and a little titanous acid, a blue mass was produced at the place where the carbon electrode was in immediate contact with the fused mass.

On treating splinters of the crystals with moderately dilute sulphuric acid, they are partially dissolved, and the undissolved portion consists entirely of alumina. In all probability, the crystals are not homogeneous, but consist of a framework of pure alumina permeated by thin layers of a sodium aluminosilicate and varying quantities of calcium, magnesium, manganese, and ferrous oxides.

The blue colour of the sapphire is also attributed to the presence of a low oxide of titanium, and this is supported by the fact that when the sapphire is heated in air it loses its blue colour and becomes brown.

The presence of ruby-red crystals in the bauxite slag has also been observed.

J. McC.

**Compounds of Aluminium Chloride with the Alkali Chlorides.** By E. BAUD (*Compt. rend.*, 1901, 133, 869—871).—The double chlorides,  $\text{Al}_2\text{Cl}_6 \cdot 2\text{NaCl}$  and  $\text{Al}_2\text{Cl}_6 \cdot 2\text{KCl}$ , have the heats of dissolution, 141.42 Cal. and 120.44 Cal. respectively, their calculated heats of formation being 11.84 Cal. and 26.38 Cal.

The compound  $\text{Al}_2\text{Cl}_6 \cdot 2\text{NH}_4\text{Cl}$ , made by fusing together its generators in the theoretical proportions, may be distilled without decomposition; its heats of dissolution and formation are 120.943 Cal. and 26.53 Cal. respectively.

*Compounds* of the type  $\text{Al}_2\text{Cl}_6 \cdot 3\text{MCl}$  are produced by employing 3 mols. of sodium or potassium chloride at  $500^{\circ}$ ; the heats of formation of the sodium and potassium salts are 15.29 and 30.53 Cal. respectively, these values being calculated from the corresponding heats of

formation, 136.97 and 112.07 Cal. The addition of the third molecule of alkali chloride to the double salt,  $\text{Al}_2\text{Cl}_6 \cdot 2\text{MCl}$ , is accompanied by a development of heat.

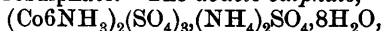
*Double salts* of the type  $\text{Al}_2\text{Cl}_6 \cdot 6\text{MCl}$  are obtained by adding the compounds  $\text{Al}_2\text{Cl}_6 \cdot 2\text{MCl}$  to the calculated quantity of fused alkali chloride. The heats of dissolution of the sodium and potassium compounds are 129.73 and 93.304 Cal. respectively, and from these values the corresponding heats of formation are calculated, namely, 19.45 and 36.636 Cal. It follows therefore that the addition of the last three mols. of alkali chloride is also accompanied by a development of heat. Thermochemical measurements indicate the existence of double salts containing even a larger proportion of alkali chloride, but the heat change is so small that it becomes impossible to determine the exact composition of these compounds.

G. T. M.

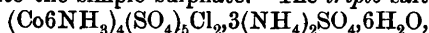
**Acid Ferric Sulphate.** By RUDOLF SCHARIZER (*Zeit. Kryst. Min.*, 1901, 35, 345—356. Compare Abstr., 1899, ii, 30; 1900, ii, 349).—The white powder obtained when a solution of ferrous sulphate is allowed to oxidise and evaporate in the air, as well as many commercial samples of ferric sulphate, contain  $\text{Fe}_2\text{O}_3 : \text{SO}_3$  in the ratio 1 : 4. This excess of sulphuric anhydride over that required for normal ferric sulphate is not due, as often supposed, to the presence of free sulphuric acid, but the substance is a definite acid salt with the composition  $\text{Fe}_2\text{S}_4\text{O}_{18}\text{H}_6 \cdot 6\text{H}_2\text{O}$ . It is prepared by adding as much ferric hydroxide as will dissolve to boiling dilute sulphuric acid, diluting, and adding sulphuric acid until the solution contains  $\text{Fe}_2\text{O}_3 : \text{SO}_3 = 1 : 4$ ; as the solution evaporates, small rhombic crystals of the salt are deposited. Part of the water is given off below  $100^\circ$ , and the remainder with some sulphuric anhydride at  $140^\circ$ . A structural formula represents the substance as a basic, acid salt,  $\text{Fe}_2(\text{OH})_2(\text{SO}_4\text{H})_4 \cdot 6\text{H}_2\text{O}$ .

L. J. S.

**Luteocobaltic Salts.** By TIMOTHÉE KLOBB (*Bull. Soc. Chim.*, 1901, [iii], 25, 1022—1031).—Luteocobaltic chloride is best prepared by dissolving cobaltous chloride and ammonium chloride in water, pouring into cold concentrated ammonia, oxidising first in the cold by means of a current of air, and then by means of lead peroxide on a water-bath. The nitrate and sulphate can be prepared by similar methods. The *acid sulphate*,  $4(\text{Co}_6\text{NH}_3)_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , prepared by the action of an excess of sulphuric acid on the normal sulphate, forms birefringent, orthorhombic, octahedral crystals, does not lose in weight when heated at  $100^\circ$ , but loses  $9\text{H}_2\text{O}$  at  $120$ — $130^\circ$ ; by crystallising from water, it is reconverted into the normal sulphate. The *chloro-sulphate*,  $(\text{Co}_6\text{NH}_3)_4\text{ClSO}_4 \cdot 3\text{H}_2\text{O}$ , forms orthorhombic prisms and is only very slightly soluble in cold water; the roseocobaltic salts do not give a chlorosulphate. The *double sulphate*,

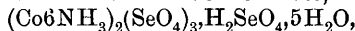


forms large, orthorhombic prisms, often several grams in weight, and loses  $6\text{H}_2\text{O}$  when left over sulphuric acid; crystallisation from water reconverts it into the simple sulphate. The *triple salt*,



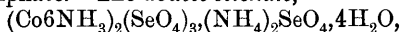
forms brilliant octahedra belonging to the cubic system, which do not lose weight at 100° but become opaque at 120°.

The *chlorochromate*,  $(\text{Co}_6\text{NH}_3)\text{CrO}_4\text{Cl}, 3\text{H}_2\text{O}$ , forms brilliant needles isomorphous with the crystals of the chlorosulphate. The *selenate*,  $(\text{Co}_6\text{NH}_3)_2(\text{SeO}_4)_3, 5\text{H}_2\text{O}$ , forms large crystals, is very soluble in water, and loses  $4\text{H}_2\text{O}$  at 100—105°. The *acid selenate*,



forms large, glistening, triclinic crystals, rapidly effloresces, loses all its water at 100—105°, and, unlike the acid sulphate, can be crystallised from water.

The *chloro-selenate*,  $(\text{Co}_6\text{NH}_3)\text{SeO}_4\text{Cl}, 3\text{H}_2\text{O}$ , forms small, glistening, striated, orthorhombic crystals isomorphous with those of the chlorosulphate. The *double selenate*,  $(\text{Co}_6\text{NH}_3)_2(\text{SeO}_4)_3, (\text{NH}_4)_2\text{SO}_4, 8\text{H}_2\text{O}$ , forms soluble, orthorhombic crystals isomorphous with those of the corresponding sulphate. The *double selenate*,



forms large, monoclinic prisms.

The *acetate*,  $(\text{Co}_6\text{NH}_3)(\text{C}_2\text{H}_3\text{O}_2)_3, 3\text{H}_2\text{O}$ , forms long prisms or hexagonal plates, which do not lose weight at 100°, but are completely dehydrated at 125°; it dissolves in less than its own weight of water at 15°, and is hygroscopic. The succinate was not obtained in a crystalline form; a *benzoate* was obtained in brilliant plates, but was not analysed.

T. M. L.

**Chromic Chloride.** By PAUL ROHLAND (*Zeit. anorg. Chem.*, 1901, 29, 159—162).—Violet chromic chloride, which is insoluble in water, remains unchanged when hydrogen is passed through the solution below 90°, but at and above this temperature transformation to the green modification and consequent solution takes place.

All the metals, except gold and platinum, effect the solution of the violet chromic chloride, and the order of the degree of influence is the same as the electromotive series of the metals.

Violet chromic chloride, when shaken with precipitated tin, passes quickly into solution. In the solution, tin ions are also to be found, because stannous chloride and chromous chloride are formed. It is doubtful whether the catalysis is to be attributed to the metal or to the chromous chloride formed.

J. McC.

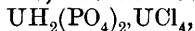
**The Number of the Blue Oxides of Molybdenum.** By G. BAILLACHE (*Compt. rend.*, 1901, 133, 1210—1213. Compare Abstr., 1901, ii, 243).—A blue substance of indefinite composition is formed when a concentrated solution of the sulphate,  $\text{Mo}_2\text{O}_5, 2\text{SO}_3$  (*loc. cit.*), is exposed to the air; an *oxide*,  $\text{Mo}_2\text{O}_3, 2\text{MoO}_4, 6\text{H}_2\text{O}$ , is obtained when the sulphate is heated with barium molybdate,  $\text{BaMoO}_4$ , and water at 100°, in a current of carbon dioxide; on evaporating the blue liquid under reduced pressure, the oxide is left as a bluish-black solid. When ordinary barium molybdate,  $\text{Ba}_3\text{Mo}_7\text{O}_{24}$ , is used, another blue *oxide*,  $3\text{Mo}_2\text{O}_3, 2\text{Mo}_7\text{O}_{24}, 18\text{H}_2\text{O}$ , is formed. With alkalis, both oxides are converted into a pale buff-coloured powder.

K. J. P. O.

**Phosphorus Molybdenum Compounds. II.** By F. MAWROW (*Zeit. anorg. Chem.*, 1901, 29, 156—158. Compare this vol., ii, 25).—The compound  $\text{Mo}_5\text{O}_{13}(\text{H}_3\text{PO}_2)_8, \text{H}_2\text{O}$ , previously described, is soluble

in water to a blue solution and gives precipitates with solutions of salts of ammonium, barium, lead, and bismuth. The barium salt has the formula  $\text{BaO}, \text{Mo}_7\text{O}_{20}, (\text{H}_3\text{PO}_4)_3, 12\text{H}_2\text{O}$ . J. McC.

**Uranium and its Compounds.** By JULES ALOY (*Ann. Chim. Phys.*, 1901, 24, [vii], 412—432).—The greater portion of this work has been already published (compare Abstr., 1899, ii, 555, 599; 1900, ii, 484; 1901, ii, 164, 244, 317). *Uranous chlorophosphate*,



separates in green crystals from a solution of uranous phosphate,  $\text{UH}_2(\text{PO}_4)_2, 5\text{H}_2\text{O}$ , in concentrated hydrochloric acid. *Uranyl iodide*,  $\text{UO}_2\text{I}_2$ , prepared by adding a slight excess of barium iodide to an ethereal solution of the nitrate,  $\text{UO}_2(\text{NO}_3)_2, 3\text{H}_2\text{O}$ , separates in red, deliquescent crystals which are very readily decomposed. *Potassium uranyl cyanide*,  $\text{UO}_2(\text{CN})_2, 2\text{KCN}$ , obtained by treating a dilute solution of uranyl acetate with a large excess of solid potassium cyanide, forms a voluminous, bulky precipitate, which subsequently changes into a mass of pale yellow prisms. G. T. M.

**Complete Freezing Point Curves of Binary Alloys.** By A. W. KAPP (*Ann. Phys.*, 1901, [iv], 6, 754—773).—Freezing point determinations have been made at intervals of 10 per cent. for each binary combination of the metals bismuth, tin, lead, and cadmium. The temperatures at which a solid separated out from the liquid alloy were determined from the halts in the cooling curve. The author finds that in no case does the eutectic alloy correspond with simple atomic proportions of the components (compare Guthrie, Abstr., 1885, 329; Miolati, Abstr., 1892, 1139; Dams, *Ann. Phys. Chem.*, 1895, 54, 486). The eutectic alloys are found to have the following composition:

Tin-bismuth	.....	56 per cent.	Bi	Cadmium-tin	70 per cent.	Sn
Lead-bismuth	.....	57	„ Bi	Lead-tin	.....	66 „ Sn
Cadmium-bismuth	60	„	Bi	Lead-cadmium	16	„ Cd.

The values given for the composition of the three eutectic bismuth alloys differ somewhat from those given by Guthrie, especially in the case of tin-bismuth. J. C. P.

### Mineralogical Chemistry.

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Graphite Deposits of Battugol. By L. JACZEWSKI (*Jahrb. Min.*, 1901, ii, Ref. 74—77; from *Explorations géol. et minières le long du chemin de fer de Sibérie*, Livre XI, 1899, 19—56). —The graphite of the Alibert mines at Battugol (Botogolskij-Golez) occurs in limestone and in nepheline-augite-syenite. Under I are the results of an analysis of the latter rock; II of the augite from the same rock (also loss on ignition, probably representing graphite, 1.63



per cent.); III of augite free from alkalis from a similar rock. Determinations of the sp. gr. and rate of combustion point to the material being mainly the graphitite of Luzi rather than graphite.

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Total.
I.	55.41	—	19.84	9.50	—	3.86	—	5.29	5.97	99.87.
II.	38.00	—	8.57	39.54	—	11.50	—	0.27	2.80	102.31.
III.	44.15	1.85	—	—	34.13	20.17	0.40	—	—	100.70.

L. J. S.

**Inflammable Gas in the Netherlands.** By J. LORÉ (*Jahrb. Min.*, 1901, ii, Ref. 84; from *Tijdschr. k. Nederl. aardrijkskundig Genotsch. Leiden.*, 1899, 35 pp.).—It has long been known that inflammable, sometimes self-igniting, gas, is exuded from the ground at many places in North and South Holland and Friesland. The sandy alluvial ground contains remains of plants and shells and there is no doubt that to these substances the gas owes its origin. Bore holes are put down to a depth of 12 to 80 metres to collect the gas, the results of two analyses of which are :

CH <sub>4</sub> .	CO <sub>2</sub> .	N.	O.	H.	CO.
97.7	10.4	9.0	0.5	0.4	—
74.8	3.4	16.2	0.4	4.6	0.6

L. J. S.

**Analysis of Manganese [Minerals] from Sardinia.** By C. RIMATORI (*Atti Real. Accad. Lincei*, 1901, [v], 10, ii, 226—232).—Analyses and physical properties of manganese minerals found in Sardinia. They are mostly varieties of pyrolusite. Two of the samples must, however, be regarded as psilomelane and one, containing 20.68 per cent. PbO, resembles a specimen of wad (Wackenrodite) from Baden. In all the specimens examined, the manganese was only present in the form of nodules or small fragments.

T. H. P.

**[Chalcopyrite and Bornite as Furnace Products.]** By ALEXANDER N. WINCHELL (*Amer. Geologist*, 1901, 28, 244—246).—The iron rails in the bed of a calciner for copper ores at Butte, Montana, become in a few months converted into chalcopyrite with which is a little bornite. Analyses are given of the chalcopyrite.

L. J. S.

**Manganosphærite, a new variety of Oligonite.** By KARL BUSZ (*Jahrb. Min.*, 1901, ii, 129—132).—The chalybite vein of the Louise mine at Horhausen, Westerwald, is intersected by a dyke of basalt, the cavities in which are partly or wholly filled with botryoidal aggregates of a fawn-brown mineral resembling sphaerosiderite in appearance. The following analysis shows, however, that the mineral differs from sphaerosiderite (FeCO<sub>3</sub>) in containing much manganese, and that in composition (3FeCO<sub>3</sub>, 2MnCO<sub>3</sub>) it agrees with Breithaupt's oligon-spar, of which crystals only have been previously described.

FeO.	MnO.	CO <sub>2</sub> .	Total.	FeCO <sub>3</sub> .	MnCO <sub>3</sub> .	Sp. gr.
36·72	24·76	38·34	99·82	59·71	40·11	3·630

Microscopical examination shows that the mineral is homogeneous, and not a mixture of rhodochrosite (MnCO<sub>3</sub>) and chalybite (FeCO<sub>3</sub>).

L. J. S.

**Altered Peridotite in Mysore.** By THOMAS H. HOLLAND (*Mem. Geol. Survey India*, 1901, 34, 1—9).—Altered peridotites in Southern India are usually penetrated by veins of white magnesite, but in the rock from Huliya now described this is not the case. Here dark gray crystals of breunnerite from half an inch to an inch across are scattered through a matrix of talc and serpentine. The breunnerite, which encloses talc, serpentine and magnetite, gave on analysis the results under I corresponding with MgCO<sub>3</sub>:FeCO<sub>3</sub>=10:1. The matrix of talc, serpentine, magnetite and a little pyrites gave II:

	SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	CO <sub>2</sub> .	H <sub>2</sub> O.	S.	Insol.	Total.	Sp.gr.
I.	—	2·93	8·27	trace	39·20	47·01	—	—	1·57	98·98	3·168
II.	42·20	13·59	—	—	30·41	5·30	7·73	0·11	—	99·34	2·853

L. J. S.

**[Datolite from] Canada.** By G. CHRISTIAN HOFFMANN (*Amer. J. Sci.*, 1901, [iv], 12, 447—448).—A compact white mineral from the Daisy mica mine, Derry, Ottawa, Co. Quebec, is proved by the following analysis, by R. A. A. Johnston, to be datolite:

SiO <sub>2</sub> .	B <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	H <sub>2</sub> O.	Total.	Sp.gr.
36·94	22·37	0·12	0·02	34·90	0·05	5·68	100·08	2·985

Associated with it is the rare mineral faujasite.

L. J. S.

**Isomorphism of Plagioclase Felspars.** By FRANZ LOEWINSON-LESSING (*Centr. Min.*, 1901, 708—709. Compare *Abstr.*, 1900, ii, 354; this vol., ii, 30).—The suggestion is put forward that albite and anorthite are not isomorphous, but form a series of double salts, and that these double salts enter into isomorphous mixture with each other, and perhaps also with the end members of the series.

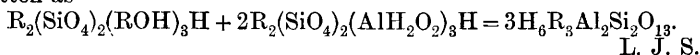
L. J. S.

**Colourless Chlorite from Aj River, Zlatoust.** By PETR A. ZEMJATSCHENSKY (*Zeit. Kryst. Min.*, 1901, 35, 357—360).—This occurs as colourless scales with hornblende and rutile in a white, crystalline, dolomitic limestone. It is optically positive, and the axial angle 2E varies from 0° to 50°. Sp. gr. 2·675—2·744 (mean 2·704). Analysis gave:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	H <sub>2</sub> O.
31·053	24·301	0·454	1·776	2·090	24·493	12·391

This chlorite is remarkable in containing very little iron, and, except in the relative amounts of alumina and magnesia, it resembles leuchtenbergite in composition. Formula, 3RO, Al<sub>2</sub>O<sub>3</sub>, 2SiO<sub>2</sub>, 3H<sub>2</sub>O, or 2CaO, 38(Mg, Fe)O, 13Al<sub>2</sub>O<sub>3</sub>, 28SiO<sub>2</sub>, 37H<sub>2</sub>O. According to Tschermak's theory of the chlorite group, the composition may be expressed

by  $\text{Sp}_4\text{At}_{13}$ , but there is a remainder of  $\text{H}_6\text{Ca}_2\text{Si}_7\text{O}_{19}$  amounting to one-tenth of the whole. According to Clarke's theory, the formula is written as



**Elæolite-syenites and Corundum-syenites in Madras.** By THOMAS H. HOLLAND (*Mem. Geol. Survey India*, 1901, 30, 169—224).—A petrographical description is given of elæolite-syenites, augite-syenites and corundum-syenites from Sivamalai in the Coimbatore district. Analysis I is of the ordinary type of elæolite-syenite. II, of large crystals, sometimes five inches across, of yellow elæolite from the coarse-grained "contemporaneous veins" of elæolite-syenite which penetrate the rock of the ordinary type. III is of large crystals of grayish felspar from these veins:

	$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	Loss on ignition.	Total.	Sp. gr.
I.	55·68	23·81	4·84	1·69	0·65	5·16	9·23	0·34	101·98	2·593
II.	43·35	34·32	1·02	0·82	—	5·52	14·62	0·75	100·40	2·62
III.	64·70	22·63	0·43	1·34	0·49	5·86	6·02	0·09	101·56	2·594

Corundum occurs as tabular, well-developed crystals in a rock consisting principally of felspar (albite and orthoclase), as in the Urals (Abstr., 1899, ii, 763) and in Eastern Ontario (Abstr., 1900, ii, 552).

L. J. S.

**The Veramin Meteorite.** By HENRY A. WARD (*Amer. J. Sci.*, 1901, [iv], 12, 453—459).—This Persian meteorite is one of the four siderolites which have been seen to fall; it fell in May, 1880, and weighs  $51\frac{1}{2}$  kilograms. It consists of 42·3 per cent. of silicates, and 57·7 per cent. of metal. Sp. gr. 4·57. The silicates present are, enstatite, olivine, possibly peckhamite, and a basic felspar. The metal has the following composition (analysis by J. E. Whitfield):

Fe.	Ni.	Co.	P.	S.	Sp. gr.
92·06	6·96	0·73	0·10	0·15	5·56

L. J. S.

**Red Rain or Blood Rain.** By NAPOLEONE PASSERINI (*L'Orosi*, 1901, 24, 325—332. Compare Abstr., 1901, ii, 322, 456).—Analysis of the red matter falling with rain on March 10th, 1901, in various parts of Italy and Central Europe shows that it consists mainly of silica, aluminium and calcium silicates, ferric oxide and organic matter ( $\text{SiO}_2$  44·3709,  $\text{CaO}$  12·3964,  $\text{Al}_2\text{O}_3$  23·6159,  $\text{Fe}_2\text{O}_3$  6·9764; organic and volatile matter 10·4677 per cent.) with small quantities of other silicates, and of carbonates, sulphates, chlorides, nitrates, &c. The red colour is due especially to the ferric oxide and organic matter.

Mineralogical examination of the matter by Giovanni D'Achiardi shows it to consist of grains, varying in size but always small; the grains are mostly of quartz, but many other minerals are also present, including felspar, pyroxene, mica, chlorite, hæmatite, calcite, or dolomite, &c. Traces of *Diatomaceæ* may also be detected. The matter is probably of cyclonic origin.

T. H. P.

## Physiological Chemistry.

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**Influence of External Temperature on Warm-blooded Animals.** By ARTHUR FALLOISE (*Trav. du lab. de L. Fredericq, Liège*, 1901, 6, 183—208; from *Arch. de Biol.*, 17, 761).—In guinea pigs, rats, and pigeons, as the temperature of the air falls from 21° to 0°, the production of carbon dioxide increases, so that it may be doubled or even tripled. Above 21°, there is also an increase, but it is not so marked. In man, the same change occurs, but in a less regular manner.

W. D. H.

**Influence of Breathing an Atmosphere rich in Oxygen.** By ARTHUR FALLOISE (*Trav. du lab. de L. Fredericq, Liège*, 1901, 6, 135—182; from *Arch. de Biol.*, 17, 713).—The absorption of oxygen, under the influence of respiring an atmosphere rich in that gas, only increases to a slight amount proportional to the quantity of oxygen which the liquids of the organism dissolve in putting themselves in equilibrium of tension with that of the oxygen of the surrounding air. This equilibrium is rapidly established, so that increase of absorption as rapidly ceases. If the tension of the atmospheric oxygen returns to the normal, the excess of oxygen previously absorbed escapes rapidly for corresponding reasons.

W. D. H.

**Respiratory Exchange during the Deposition of Fat.** By MARCUS S. PEMBREY (*J. Physiol.*, 1901, 27, 407—417).—During the autumn, the marmot feeds eagerly on carbohydrate food and rapidly deposits fat in its body as a reserve for combustion during its winter-sleep. The respiratory quotient  $\text{CO}_2:\text{O}_2$  is greater than unity; the mean of 22 determinations is 1.21, the maximum being 1.39, the minimum 1.04. These high quotients cannot be explained by a reduction in the absorption of oxygen, for, compared with the condition during fasting, there is a considerable increase. The probable explanation is that suggested by Hanriot: during the formation of fat from carbohydrates, a considerable quantity of carbon dioxide is split off from the carbohydrate molecule.

W. D. H.

**Influence of Occlusion of the descending Aorta on the Respiratory Exchanges.** By HECTOR RULOT and LÉON CUVELIER (*Trav. du lab. de L. Fredericq, Liège*, 1901, 6, 9—20; from *Arch. de Biol.*, 15, 629).—Bohr and Henriques (*Arch. de physiol.*, 1897) have stated that occlusion of the thoracic aorta exercises no influence on the respiratory exchange; they therefore conclude that the main seat of combustion in the body is not in the tissues and organs of the body, but in the lungs, thus carrying one back to the ideas which prevailed in the time of Lavoisier. The present experiments on dogs show that these ideas have no foundation. The greater the portion of the body shut off from the circulation, the less is the sum total of the respiratory interchanges. At the highest level of occlusion, these were

reduced to a half of the normal. The respiratory quotient rises during occlusion ; after occlusion, it generally falls but sometimes rises.

W. D. H.

**Carbon Dioxide as an Excitant of the Respiratory Centre.** By HECTOR RULOT and LÉON CUVELIER (*Trav. du lab. de L. Fredericq, Liège*, 1901, 6, 1—8 ; from *Arch. de Biol.*, 15, 621).—The symptoms produced by excess of carbon dioxide are very similar to those caused by diminution of oxygen, and some observers doubt whether carbon dioxide is really an excitant of the respiratory centre. The present experiments confirm the classical theory that the gas is an excitant of the respiratory centre, which has also been recently stated to be the case by Zuntz and Loewy (*Arch. f. Physiol.*, 1897, 379—390).

W. D. H.

**Changes in the Composition of Gas injected into the Subcutaneous Tissues.** By LÉON PLUMIER (*Trav. du lab. de L. Fredericq, Liège*, 1901, 6, 77—98 ; from *Arch. de Biol.*, 16, 323).—Gases introduced into the subcutaneous tissues are absorbed especially quickly in the case of those soluble in the blood. Before absorption, the gases tend to put themselves in equilibrium of tension with the blood gases, and this equilibrium is soonest reached in the case of gases which are most soluble in the blood. The oxygen tension in the blood of the subcutaneous region is equal to 6—8 per cent. of an atmosphere, the corresponding number for carbon dioxide is 5 to 8, and for nitrogen 80 per cent. If the gas injected contains a high percentage of carbon dioxide and oxygen, the tension of the oxygen becomes temporarily greater than that of the oxygen of the atmosphere ; this is simply because the carbon dioxide is more rapidly absorbed than the oxygen.

W. D. H.

**The Gases in Blood at Different Altitudes during a Balloon Ascent.** By J. TISSOT and HALLION (*Compt. rend.*, 1901, 133, 1036—1038. Compare this vol., ii, 92).—Experiments made with the blood of a dog during the ascent of a balloon to a height of 3500 metres and its subsequent descent, the results being corrected for the action of air on the collected blood between the time of its withdrawal from the animal and the analysis, show that the power of hæmoglobin to combine with oxygen increases somewhat with a reduction of pressure, at any rate up to the altitude stated. On the level, 100 c.c. contained 15·5 c.c. of oxygen, at 3500 metres, 19·97 c.c., and at 800 metres during the descent, 15·7 c.c. The variations in the quantity of carbon dioxide in the blood are in the opposite direction to those required by the laws of the dissolution of gases, whereas the nitrogen behaves as if it were simply dissolved, 100 c.c. of blood containing 3·25 c.c. at the level and only 0·525 c.c. at 3500 metres. The total quantity of gases contained in the blood increases with the altitude, and the quantities of carbon dioxide and oxygen likewise increase with the altitude. The pressure of the blood in the femoral artery of the dog remained constant throughout the ascent.

C. H. B.

**Sugars of the Blood and Glycolysis.** By RAPHAEL LEPINE and BOULUD (*Compt. rend.*, 1901, 133, 720—721).—Horse's blood possessing the same reducing power as dog's blood is less dextrorotatory or may even be levorotatory. This is due to conjugated glycuronic acid.

If dog's blood is kept for an hour at 39° while oxygen is passed through it, the fermentable sugar disappears, and the dextrorotatory power decreases or the levorotatory power increases. This is believed to be due to the glycolysis of the sugar, and the appearance of conjugated glycuronic acid. The presence of chloroform somewhat hinders the change.

W. D. H.

**Physiology of the Gill, and Osmotic Pressure of the Blood in the Crayfish.** By LÉON FREDERICQ (*Trav. du lab. de L. Fredericq, Liège*, 1901, 6, 61—63; from *Bull. de l'Acad. roy. de Belg.*, 1898, [iii], 35, 831—833).—The amount of salt in crab's blood can be increased or lessened by altering the amount in the water in which they live. It is quite different in the fresh-water crayfish. Although the gill membrane is so thin, it does not play the inert rôle of a membrane in a dialyser, but is a barrier which effectually separates the internal medium, the blood, from the external, so far as salts are concerned, although it is naturally traversed by the gases of respiration. The osmotic tension of the blood is equal to that exerted by a 1.3 per cent. solution of sodium chloride ( $\Delta = 0.8^\circ$ ); this is higher than is found in vertebrate blood.

W. D. H.

**Artificial Parthenogenesis.** By JACQUES LOEB, MARTIN FISCHER, and HUGH NEILSON (*Pflüger's Archiv*, 1901, 87, 594—596. Compare Abstr., 1900, ii, 608; 1901, ii, 177).—Further experiments in support of those previously published.

W. D. H.

**Artificial Parthenogenesis.** By ARTHUR W. GREELEY (*Amer. J. Physiol.*, 1902, 6, 296—304).—After maturation has been completed, the unfertilised eggs of the starfish, *Asterias forbesii*, can be made to develop regularly into bipinnaria by an exposure to a temperature of 4° to 7° for from 1 to 9 hours. Segmentation of the *Asterias* egg cannot be produced by raising the temperature of the sea-water.

W. D. H.

**Prolongation of the Life of Sea Urchins' Eggs by Potassium Cyanide.** By JACQUES LOEB and WARREN H. LEWIS (*Amer. J. Physiol.*, 1902, 6, 305—317).—The life of the unfertilised eggs of the sea urchin can be materially prolonged by adding to the sea-water a small quantity of potassium cyanide. Sexual as well as parthenogenetic development is prolonged. Lack of oxygen has little or no influence. So long as death is considered as something merely negative (namely, the cessation of life processes), it must appear paradoxical that a deadly poison will prolong life. The paradox disappears if it is assumed that certain active (mortal) processes occur so as to cause death. These specific processes (possibly enzymatic) are in unfertilised eggs checked or modified by sexual or osmotic fertilisation, and also by potassium cyanide, which substitutes for the destructive action of these processes a condition of suspension of life.

W. D. H.

**Eggs of *Rana Temporaria*.** By HEINZ KOLB (*Chem. Centr.*, 1901, ii, 1233; from *Inaug. Diss.-Zurich*, 1901).—The amount of glycogen, water, sulphur, phosphorus, and fat were estimated at different periods during the development of the eggs of the common frog. Glycogen shows periodical variations, being at its minimum when the egg is ripe. Sulphur increases, and phosphorus diminishes, during development; fat shows a slight increase, water a marked one. W. D. H.

**Composition of Egg-Yolk.** By JOHN MALCOLM (*J. Physiol.*, 1901, 27, 356—359).—The percentages of proteid, fat, and phosphorus in the yolk of eggs from the same hen are in close agreement. There are, however, very considerable differences in eggs from a number of hens, even of the same breed. The percentage of lecithin varies considerably. Analytical details are given [compare Thorpe, this vol., ii, 95]. W. D. H.

**The Osmotic Pressure of Dog's Submaxillary Saliva.** By PIERRE NOFL (*Trav. du lab. de L. Fredericq, Liège*, 1901, 6, 225—239; from *Arch de Biol.*, 18).—The osmotic pressure of the submaxillary saliva of the dog, obtained by stimulation of the chorda tympani is variable ( $\Delta = 0.193$ — $0.396$ ). The saliva from the same gland, secreted spontaneously, is more dilute ( $\Delta = 0.109$ — $0.266$ ). The tension is due all but exclusively to the salts of the saliva. The osmotic tension rises when the duct is obstructed; this is explicable by supposing that absorption of water occurs in the excretory tubules W. D. H.

**Conversion of Pancreatic Zymogens into Enzymes.** By HORACE M. VERNON (*J. Physiol.*, 1901, 27, 269—322).—Extracts of fresh pancreas show usually no ferment activity for some days, and then suddenly develop nearly their maximum power. After maintaining this power for some days or weeks, they gradually deteriorate. When the glands from several animals are minced together and extracted, the ferment activity begins to develop at once. As regards trypsin, glycerol extracts are the most powerful; the rennetic value is but little influenced by the nature of the extracting liquid. As a rule, however, tryptic and rennetic values vary together. Diluting glycerol extracts with water develops tryptic power increasing with the degree of dilution. The conversion of zymogens with enzyme is enormously increased by the addition of an active extract. It is the tryptic ferment which liberates both the ferments. The products of tryptic digestion have the same power to a less degree. Bubbling oxygen or carbon dioxide through the glycerol extract at  $38^{\circ}$  has no influence, but if active extract is added as well, oxygen increases, and carbon dioxide diminishes, enzyme formation. In order to obtain an active tryptic extract, the plan advised is to use pig's pancreas, and extract it with 50—75 per cent. glycerol and test its proteolytic power every few days. After it has risen considerably, and before much auto-digestion has occurred, the glycerol should be filtered off and kept separate. Its activity would still further increase, and then remain nearly constant for months and perhaps years. One part of the

finely minced gland, and four parts of the extracting liquid by volume should be employed.

W. D. H.

**Production of the Tryptic Ferment from its Zymogen.** By HENRY F. BELLAMY (*J. Physiol.*, 1901, 27, 323—335).—The dog's pancreas presents two phases of activity; (1) a slow and continuous one, feebly evident after digestion, and reaching its height during complete fast; during this period, the principal material in the gland cells is zymogen: (2) a rapid and intermittent phase coincident with the period of gastric activity, in which, as advocated by Herzen, the inactive zymogen receives an 'internal secretion' from the spleen, which liberates the trypsin. The blood is the vehicle by means of which this is conveyed to the pancreas; it is not present in the serum; if it is in the plasma, it is destroyed when the blood clots; it probably is conveyed by the blood corpuscles. If a dog is deprived of its spleen, no trypsin is formed, but trypsinogen continues to be formed and is secreted as such; it can, however, be rendered useful by subsequent conversion into trypsin by an agency other than splenic, namely, by the secretion of the mucous membrane of the small intestine, especially of the jejunum.

W. D. H.

**Proteolytic Enzyme of the Thymus.** By FR. KUTSCHER (*Zeit. physiol. Chem.*, 1901, 34, 114—118).—The thymus gland contains a proteolytic enzyme, which leads to auto-digestion in extracts of the gland. Among the products of proteolytic action, ammonia and lysine are found; arginine, aspartic acid, glutamic acid and tyrosine are absent. The presence of histidine and leucine is doubtful. Whether this action is due to trypsin, or to another hitherto unknown enzyme, is for the present left uncertain.

W. D. H.

**Nutrition of the Suckling Infant.** By KARL OPPENHEIMER (*Zeit. Biol.*, 1901, 42, 147—160).—The varying needs of an adult for food are comparatively easy to understand. It is more difficult to realise why infants during suckling, in which the amount of muscular exercise is uniformly small, should also take different amounts of food. The amount of milk taken may be ascertained by weighing the child before and after each meal. In cases previously recorded, the total milk sucked during the first ten weeks of life varies from 30 to 53 kilograms. In the present paper, careful observations are given in connection with a child prematurely born at the eighth month, and the results are compared with the figures previously given by others, and an attempt made to find a general rule to account for the variations. In two children, there was a constant relation between amount of food and body weight, but this does not hold throughout. The constant relationship is between food and body surface (Rubner's law).

W. D. H.

**Energy Value of Diet in Man.** By MAX RUBNER (*Zeit. Biol.*, 1901, 42, 261—308).—A general view is given of the author's well known work on this subject. The nutrition value of a few important food stuffs is as follows: meat, 76·8; bread, 82·1; milk, 89·8; potatoes,



92·1. These numbers are the percentage of the total energy available for use in the body. These and other numbers are employed to reckon the value of mixed dietaries. The facts given are mainly statistical.

W. D. H.

**The Physiological Significance of Salt.** By LÉON FREDERICQ (*Trav. du lab. de L. Fredericq, Liège*, 1901, 6, 64—66; from *Bull. de l'Acad. roy. de Belg.*, 1898, [iii], 35, 834—836).—Bunge states that sodium chloride is chiefly used by those who take abundance of vegetable food in order to combat the harmful influence of potassium salts which predominate in vegetables and which would otherwise tend to replace the sodium salts of the blood and tissues. Lapique, on the other hand, believes that the function of salt is simply to accentuate the flavours of foods, and that this purely gustative action can equally well be carried out by salts of other metals. The observations recorded in the present paper support the latter view. An examination of the salt prepared by the natives of the Congo State by burning aquatic plants show it to consist mainly of potassium chloride and sulphate.

W. D. H.

**Action of Alcohol on Man.** By R. O. NEUMANN (*Arch. Hyg.*, 1901, 41, 85—118).—Polemical against Rosemann. The author maintains his original contention that alcohol acts as a proteid-sparer.

W. D. H.

**The Value of Rhamnose in the Animal Organism.** By MAX CREMER (*Zeit. Biol.*, 1901, 42, 428—467).—The paper is largely concerned with theoretical considerations on carbohydrate metabolism. One of the most important is the assertion, which rests on experimental proofs, that proteids which are free from a carbohydrate radicle do not lead to glycogen formation. Rhamnose does not lead to glycogen formation, but comparatively small amounts leave the body as such. It has a calorific value, and its combustion leads to a sparing effect on other constituents of the body, especially of fat. Numerical data of experiments on one dog and four rabbits, mainly relating to gaseous metabolism, are given.

W. D. H.

**The Origin of Glycogen from Proteid.** By BERNHARD SCHÖNDORFF (*Pflüger's Archiv*, 1901, 88, 339—345).—Polemical. A reply to Cremer.

W. D. H.

**Behaviour of Xylan in the Animal Body.** By B. SLOWTZOFF (*Zeit. physiol. Chem.*, 1901, 34, 181—193).—In rabbits, if xylan is given with the food, part is absorbed (33 to 83 per cent.), and the remainder passes away with the fæces. A small portion (1·5 to 4·6 per cent.) of that which is absorbed appears in the urine; the rest is used by the organism, although it is uncertain if this has any nutritive value. The urine contains a furfuraldehyde-forming substance of undetermined composition. If the animal is killed a short time after injection of xylan, that material is found in the blood, liver, and muscles. Xylan undergoes putrefaction, but not so readily as xylose; its destruction in the intestines by putrefactive agencies is improbable.

W. D. H.

**Changes in the Carbohydrates in the Body of *Ascaris*. An Animal Fermentation Process.** By ERNST WEINLAND (*Zeit. Biol.*, 1901, 42, 55—90).—The author has previously called attention to the large amount of glycogen in the body of various parasitic worms. It often amounts to from a third to nearly a half of the total dry material. The present experiments were made on the common round worm *Ascaris*. This animal requires no free oxygen, and can be kept alive in boiled saline solution for several days; bubbling oxygen through the salt solution does not prolong its life; but bubbling carbon dioxide through the solution almost doubles its period of life. The daily loss per 100 grams of body weight is 0.7 gram of glycogen, 0.1 gram of dextrose, and 0.07 gram of nitrogen. The relative amount of water to solids increases, but the fat undergoes practically no change. The normal alkalinity of the animal's tissues diminishes, and may even be replaced by faint acidity. The daily production of carbon dioxide (during hydrogen respiration) is 0.38 gram per 100 grams of body weight. The animal acquires a rancid odour, and this is due to two fatty acids, butyric and valeric, 0.3 gram of valeric acid being produced daily for every 100 grams of body weight; this is not due to micro-organisms, but is a product of the animal's metabolism. The nitrogen found in the salt solution in which the animal lives amounts to 0.0015 gram per 100 grams of body weight daily; the form in which the nitrogen leaves the body was not ascertained. On comparing the loss of weight to the products excreted, the former is found to be the greater; probably some of the lost material is used in the production of ova and spermatozoa. Provisional formulæ are given to account for the breakdown of carbohydrate material. Particular attention is drawn to the fact that this breakdown is not oxidation, but an action of a fermentative nature similar to that which occurs in certain micro-organisms and fungi.

W. D. H.

**Formation of Fat from Carbohydrate.** By KARL B. LEHMANN and ERWIN VOIT (*Zeit. Biol.*, 1901, 42, 619—671).—The experiments show that a carbohydrate diet causes a considerable but variable putting on of carbon in the body.

W. D. H.

[**Fat Absorption.**] By EDUARD PFLÜGER (*Pflüger's Archiv*, 1901, 88, 299—338, 431—452).—These are two further contributions to a much debated question. Details are given regarding the melting points of fatty mixtures; the existence of a form of oleic acid in horse's fat with a high iodine number; the solubilities of fats and fatty acids in various mixtures of bile and sodium carbonate; the importance of sodium carbonate for the bringing of oleic and other fatty acids into a form which is soluble in water; the importance of the bile circulation both for the digestion and absorption of fat, and, in the second paper, the importance of the presence of soaps for enabling fatty acids to enter into solution.

W. D. H.

**The Physiological Proteid Minimum.** By MAX CREMER and M. HENDERSON (*Zeit. Biol.*, 1901, 42, 612—617).—Two experiments are described on dogs, which are similar to those performed by E. Voit

and Korkunoff (*Zeit. Biol.*, 32, 58). The extreme values given by these authors were not obtained.  
W. D. H.

**Proteid Metabolism.** By MAX GRUBER (*Zeit. Biol.*, 1901, 42, 407—427).—The subject of proteid metabolism is treated mainly from the theoretical standpoint; Pettenkofer and Voit's old distinction between the organ proteid, which undergoes but little and that a constant change, and the proteid derived directly from the food, which is subject to great variations, is insisted on. The influence of water in increasing the excretion of waste nitrogenous products, and the fact that different proteids after absorption vary in their yield of katabolic products, are supported by experiments.  
W. D. H.

**Decomposition of Proteids in Men during the Performance of Hard Work.** By C. JACKSON (*Atti Real. Accad. Lincei*, 1901, [v], 10, ii, 186—188).—The author has compared the urine of five persons while at rest and while undergoing vigorous exercise on a mountain climb. The results are given in the following table: (1) was a porter of 35 years; (2), (3), and (4) men of 26, 32, and 62 years respectively; and (5) a youth of 17 years:

	Specific gravity.		Total nitrogen.		Nitrogen as urea and ammonia.		Ratio of nitrogen as urea and ammonia to total.	
	Resting.	Work-ing.	Resting.	Work-ing.	Resting.	Work-ing.	Resting.	Work-ing.
(1)	1024	1023	0·78	1·28	0·65	0·99	0·83	0·77
(2)	1023	1028	1·41	1·65	1·13	0·92	0·80	0·56
(3)	1024	1024	1·14	1·79	0·94	1·18	0·82	0·66
(4)	1021	1026	1·43	1·65	1·27	0·69	0·88	0·42
(5)	1023	1030	1·51	2·11	1·32	1·82	0·87	0·86

Thus in all cases, more nitrogen was eliminated in the urine during work, a fact perhaps depending to some extent on the increased amount of food taken; (1) and (5) ate very well, whilst (4) took scarcely any food. Except for (5), the proportion of the total nitrogen present as urea was diminished by working. It is probable that fatigue is a pathological condition in which the matter eliminated from the body is not only increased, but changes in a manner that indicates a solution of the tissues, probably of the muscles. By exercise, the same work becomes possible without destruction of the muscles.  
T. H. P.

**The Change produced in Albumoses by the Gastric Mucous Membrane.** By KARL GLAESSNER (*Beitr. chem. Physiol. Path.*, 1901, 1, 328—338).—A regeneration of proteid from its hydrolytic products occurs in the gastric mucous membrane; this, however, relates exclusively to the albumoses. The change in the dog commences soon after

digestion starts, reaches its maximum five or six hours later, and then subsides. This power of proteid synthesis is a property of the mucous membrane. It is not considered that rennin plays any part in the process; the formation of plastein by rennin *in vitro* is probably not analogous to what occurs *in vivo*. W. D. H.

**Nutritive Value of Gelatin.** By OTTO KRUMMACHER (*Zeit. Biol.*, 1901, 42, 242—260).—The heat-value of gelatin, as obtained by the use of the calorimeter, was found to be 5·3676 Cal. in one preparation, 5·3779 in another. In order to obtain its physiological heat value, several deductions have to be made, principally for unburnt products in urine and fæces; after the deductions, the heat value is 3·8835 Cal., or 72·35 per cent. of the total energy; Rubner's numbers for meat and proteid are 74·9 and 76·8 per cent. respectively. In experiments on dogs, the proteid decomposition during gelatin feeding is 62·6 per cent. of that which is broken down during inanition. This probably represents the maximal action of gelatin. In a man of mean body weight, the amount of proteid which undergoes katabolism per diem is 70 grams. If gelatin is given to exert the maximal effect, it being assumed that the same relationship holds for man as for dogs, 33 grams of gelatin will reduce the katabolised proteid to 56 grams, or 33 grams of gelatin will spare 14 grams of proteid. W. D. H.

**The Nutritive Value of Meat and Meat Preparations in Man.** By WILHELM PRAUSNITZ (*Zeit. Biol.*, 1901, 42, 377—406).—A research carried out in the usual manner, in which the utility of various forms of meat food is compared. The main result is that fresh meat cooked in the usual way is much more easily digested than various preparations in which drying of the meat is part of the method employed. Roast fresh meat is almost entirely absorbed, and leads to only a small formation of fæces. Among the various patent preparations, there are differences, but in every case the amount of fæces is large, and contains much unused nutriment. W. D. H.

**The Place of Purine Substances in Metabolism.** By OTTO LOEWI (*Pflüger's Archiv*, 1901, 88, 296—298).—Polemical against Burian and Schur (this vol., ii, 33). W. D. H.

**Relationship of Iron and Pigments in the Liver and Skin.** By N. FLORESCO (*Compt. rend.*, 1901, 133, 828—830).—From observations made at first on snails, but later on dogs, cats, and rabbits, the conclusion is reached that there is a relation between the liver and the skin and also the fur, in point of view of the amount of iron and of pigments. The liver, and the skin of dark-coloured animals contain nearly double the quantity of iron and of pigment which those with white fur possess. Intermediate cases occur in those lightly-coloured. W. D. H.

**The Ammonia removing Function of the Liver.** By ARTHUR BIEDL and HEINRICH WINTERBERG (*Pflüger's Archiv*, 1901, 88, 140—199).—The statement made by previous observers that the blood

entering the liver contains more ammonia than that which leaves it is confirmed. The power of the liver to remove ammonia is in the present research investigated on animals which have been poisoned by ammonia and certain ammonium salts. In some experiments, the liver was thrown out of gear by an Eck's fistula. The liver appears to be able to cope with increased quantities of ammonia produced in certain pathological states; the proof is not, however, clear that this alone will explain the autointoxication produced when the liver is thrown out of the circulation.

W. D. H.

**Formation of Free Iodine from Iodoform.** By FRITZ ALTENBERG (*Chem. Centr.*, 1901, ii, 1212; from *Arch. int. Pharmacodyn. Ther.*, 8, 106).—Urine, blood, and pus cannot decompose iodoform with the formation of free iodine. Cellular organs in the absence of micro-organisms can do so, however; this power is especially found in secreting glands, particularly the testis.

W. D. H.

**Formation of Ethereal Sulphate in the Animal Body.** By GUSTAV EMBDEN and KARL GLAESSNER (*Beitr. chem. Physiol. Path.*, 1901, 1, 310—327).—The experiments were performed on dogs by the perfusion method. The liver was found to be the principal place where the synthesis leading to the formation of ethereal sulphates takes place. They are not formed by the muscles or intestine, but small quantities are manufactured by the kidneys and lungs.

W. D. H.

**Effect of Freezing on Milk.** By FRED. BORDAS and SIG. DE RACZKOWSKI (*Compt. rend.*, 1901, 133, 759—760).—On freezing milk, the upper portion of the block is soft and contains most fat; the peripheral portion is transparent; the centre forms a white nucleus and is chiefly casein and sugar; the lower portion contains even a larger proportion of casein and sugar. The following are the analyses (per cent.) of the four portions:

	Peripheral.	Upper.	Central.	Lower.
Ash .....	0.46	0.61	2.10	2.78
Fat .....	1.54	21.68	1.58	0.79
Lactose.....	2.81	3.52	10.64	18.65
Casein .....	1.72	6.40	12.43	19.31

W. D. H.

**The Diurnal Curve of Sweat Formation.** By LÉON FREDERICQ (*Trav. du lab. de L. Fredericq, Liège*, 1901, 6, 209—212).—By determinations on the author's own person, it is shown that the curve of sweat formation in the day very accurately follows that of the diurnal changes of temperature. The increased formation of sweat during muscular activity is mainly due to elevation of the internal body temperature. The rise of temperature acts on the nervous centres concerned in the process.

W. D. H.

**Estimation of Acidity in Urine.** By ROBERT ARNSTEIN (*Zeit. physiol. Chem.*, 1901, 34, 1—27).—The methods investigated were those

of Freund-Lieblein and of Jäger. The influence of various salts on the acidity is also studied. Further investigation in order to find an accurate method is promised.

W. D. H.

**Investigation of Fæces.** By HANS URY (*Chem. Centr.*, 1901, ii, 1233—1234; from *Deutsch. med. Woch.*, 27, 718—723).—The paper mainly relates to methods, and especially to those which have for their object the estimation of nitrogen, phosphorus, and nuclein in the fæces.

W. D. H.

**Reactions of Infusoria with Carbonic and other Acids.** By HERBERT S. JENNINGS and E. M. MOORE (*Amer. J. Physiol.*, 1902, 6, 233—250).—Many infusoria collect in solutions of carbon dioxide and other acids, just as *Paramæcium* does. The spontaneous collections formed by these organisms may therefore be due to their excretion of carbon dioxide; nevertheless there are other infusorians which, although they form spontaneous collections, do not gather in acids, and others still which undoubtedly produce carbon dioxide, but do not form spontaneous collections at all.

W. D. H.

**Transformation of Glycerol into Sugar by Testicular Tissues.** By GABRIEL BERTRAND (*Compt. rend.*, 1901, 133, 887—890).—The testicular tissues, obtained under aseptic conditions from the dog, rabbit, guinea-pig, and cock, do not transform glycerol, in 10 per cent. aqueous solution, into a reducing sugar. The change is brought about by the addition of a trace of a solution containing microbes. The sugar obtained under these conditions reduces Fehling's solution in the cold and is identical with dihydroxyacetone yielding the osazone melting at 130° (compare Berthelot, *Ann. Chim. Phys.*, 1857, 369).

G. T. M.

**Cyclic Terpenes and Camphor in the Animal System. I.** By EMIL FROMM and HERMANN HILDEBRANDT (*Zeit. physiol. Chem.*, 1901, 33, 579—594. Compare Schmiedeberg and Meyer, *ibid.*, 3, 422; Pellacani, *Arch. exp. Path. and Pharm.*, 1883, 17, 376; Schmiedeberg, *ibid.*, 1881, 14, 308; Rimini, *Rend. Accad. Lincei.*, [v], 10, 244).—Cyclic terpenes and camphors are transformed in the animal system, by a process of oxidation or hydration, into monohydroxyl derivatives, which are eliminated in the form of glycuronic acid derivatives.

When a hydroxyl group is already present, as in sabinol, the compound of the original substance with glycuronic acid is eliminated. Pinene yields *pinenolglycuronic acid*, but neither acid nor salts have been obtained in a crystalline form; on treatment with hydrochloric acid, it yields a hydrocarbon,  $C_{10}H_{14}$ , boiling at 175—176°.

*Phellandrenolglycuronic acid* and its salts are non-crystalline and when hydrolysed yield a *phenol*,  $C_{10}H_{14}O_2$ , melting at 142°, and a hydrocarbon,  $C_{10}H_{14}$ , distilling at 175°.

*Camphenolglycuronic acid*, on hydrolysis, yields camphenol,  $C_{10}H_{15}\cdot OH$ , boiling at 202—204°.

*Sabinolglycuronic acid* yields cymene on hydrolysis, and on oxidation, gives a mixture of two acids, the one melting at 220°, and the other remaining solid even at 320°.

*Sabinolglycuronic acid*, on hydrolysis, yields cymene and on oxidation gives benzoic acid together with an acid,  $C_{11}H_{10}O_4$  or  $C_{14}H_{14}O_5$ , melting at 198°.

*Thujonehydrateglycuronic acid* yields a crystalline potassium salt,  $C_{16}H_{25}O_8K$ , which on hydrolysis yields glycuronic acid and a hydrocarbon boiling at 170—180°. J. J. S.

**Borneol- and Mentholglycuronic Acids.** By A. BONANNI (*Beitr. chem. Physiol. Path.*, 1901, 1, 304—309).—In dogs, if borneol is given by the mouth, it is excreted in the urine in combination with glycuronic acid. The same is true for menthol.

Borneolglycuronic acid,  $C_{16}H_{26}O_7 \cdot H_2O$ , which crystallises in needles, is soluble in water, alcohol, ether, acetone, or chloroform; when boiled with dilute sulphuric acid, it is resolved into its components. The potassium, zinc, and copper salts are crystalline, the calcium and barium salts amorphous.

Mentholglycuronic acid was only obtained as a syrup, neither could crystalline salts be obtained. W. D. H.

**Certain Biological Characters of Phenylhydrazine.** By LOUIS LEWIN (*Zeit. Biol.*, 1901, 42, 107—146).—Chemists who work much with phenylhydrazine suffer from ill-health, of which the most prominent sign is a kind of eczema. The substance is also poisonous to animals, and the pathological signs produced are described in full. Particular attention is directed to the action on the blood; especially on living blood; here a green derivative of hæmoglobin, called hæmo-verdin, is produced (compare this vol., i, 67). W. D. H.

**Metabolism in Acute Gout.** By HANS VOGT (*Chem. Centr.*, 1901, ii, 1212; from *Arch. klin. Med.*, 71, 21—28).—In gout, there is retention of nitrogen, which is not due to putting on of flesh. It appears to be explained by katabolism of nuclein, the phosphorus of which is excreted and the nitrogen retained. Whether this is purine nitrogen or proteid nitrogen must be decided by further work on the fate of uric acid and purine during the gouty condition. If nuclein is given in the food, it appears to be absorbed and excreted normally, the phosphorus soon, the uric acid later. W. D. H.

**Peptone in the Urine.** By MIDORI ITO (*Chem. Centr.*, 1901, ii, 1212—1213; from *Arch. klin. Med.*, 71, 29—36).—Some rare cases are described in which true peptone (in Kühne's sense) was found in the urine. The cases were those of lung disease. W. D. H.

**Alcaptonuria.** By FRANZ MITTELBACH (*Chem. Centr.*, 1901, ii, 1213; from *Arch. Klin. Med.*, 71, 50—72).—The theory that alcapton originates from tyrosine is confirmed. Phenylpropionic acid does not influence the excretion, phenylacetic acid does. In the estimation of alcapton, it is necessary to remove the uric acid first by saturation with ammonium chloride. W. D. H.

**Compounds of Arsenic in the Human Liver.** By RICHARD VON ZEYNEK (*Chem. Centr.*, 1901, ii, 1232; from *Centr. f. Physiol.*, 15, 405—408).—In arsenic poisoning (two cases), arsenic was found in a 0.1 sodium carbonate extract of the liver and in the insoluble residue after extraction with 10 per cent. solution of sodium chloride. After peptic digestion, the arsenic is found in the insoluble residue [Slowtzoff made similar observations (this vol., ii, 34)]. W. D. H.

**Excretion of Cacodylic Acid and its Detection in Cases of Poisoning.** By DIOSCORIDE VITALI (*Chem. Centr.*, 1901, ii, 1212; from *Boll. Chim. Farm.*, 40, 657—665).—Cacodylic acid is sometimes used therapeutically; it passes as such into the urine, and not in an organic compound. A method of detecting it in the urine is described. W. D. H.

**The Influence of Carbon Monoxide on the amount of Carbon Dioxide in Arterial Blood.** By T. SAIKI and G. WAKAYAMA (*Zeit. physiol. Chem.*, 1901, 34, 96—107).—The experiments were made on rabbits and dogs. Under the influence of carbon monoxide poisoning, the amount of oxygen and carbon dioxide in the blood is greatly diminished; the amount of lactic acid increases. Amyl nitrite has the same effect on the carbon dioxide. W. D. H.

**The Influence of Certain Poisons on the Synthesis of Phenol-sulphuric Acid in the Animal Organism.** By K. KATSUYAMA (*Zeit. physiol. Chem.*, 1901, 34, 83—95).—In rabbits, poisoning with carbon monoxide produces an increase of the combined sulphates. The reaction of the urine, which is normally alkaline in these animals, becomes acid or neutral. Amyl nitrite inhibits the formation of phenol-sulphuric acid. W. D. H.

**Metabolism during Curare-poisoning.** By OTTO FRANK and FRITZ VOIT (*Zeit. Biol.*, 1901, 42, 309—362).—Metabolism pursues the same course when the muscular system is rendered inactive by curare. Large doses of curare upset metabolism, mainly by paralysing the muscular portion of the circulatory system and lowering blood-pressure; the lessening of the metabolism which then occurs is partly due to lowering of the body temperature. When a moderate dose is given so that only the voluntary muscles are affected, metabolism is so regular that the smallest changes produced by other agencies are markedly noticeable.

The total metabolic exchanges are probably in the main greater in a curarised animal than in one simply at rest, in order to maintain the normal body temperature. Curarised animals, except during lactation, follow Rubner's law of a fixed relationship between surface area and the amount of katabolism. About 85 per cent. of the total heat produced comes from fat metabolism. The metabolism both of proteid and fat in curarised, and in absolutely resting animals, is almost the same as under normal conditions. W. D. H.

**Toxicological Studies on the Selachian Heart.** By WALTHER STRAUB (*Zeit. Biol.*, 1901, 42, 363—376).—Observations are recorded



regarding the action of antiarin and strophanthin on the heart of the ray, dogfish, and other selachians, and the results compared with those found in experiments with the frog's heart (*Arch. exp. Path. Pharm.*, 1901, 45, 346).

These digitalis glucosides show, towards the fishes' heart, a smaller toxicity than in the frog; the effect on auricle and ventricle is about equal.

W. D. H.

**Ergot of Rye.** By MARCEL GUÉDRAS (*Compt. rend.*, 1901, 133, 1314).—The therapeutic action of ergot of rye is due to sphacelinic acid, cornutine, and the salts formed by their combination. Their separation presents great difficulty because their solubilities are practically equal. A good sample of ergot should contain a high percentage of sphacelinic acid and cornutine, and a low percentage of sclerotic acid and other inert substances.

C. H. B.

**Physiology of the Hypophysis.** By E. VON CYON (*Pflüger's Archiv*, 1901, 87, 565—593).—Hypophysin (not chemically identified) is placed with thyroiodin and suprarenin (or epinephrin) as a physiological heart poison. Removal of the hypophysis interferes with general metabolism, and produces not only acromegaly but also sterility. The main part of the paper has but little chemical interest.

W. D. H.

**Phloridzin Diabetes.** By GRAHAM LUSK (*Zeit. Biol.*, 1901, 42, 31—44. Compare Abstr., 1900, ii, 558).—In phloridzin diabetes, no sugar originates from fat. The number of calories which are lost by the excretion of sugar are made good by the increased decomposition of proteid. The relationship between dextrose and nitrogen in the urine of the fasting phloridzin diabetic dog is 3.75 : 1; in the rabbit, goat, and cat, it is 2.8 : 1.

W. D. H.

**The Influence of Valency in the Antitoxic Action of Ions.** By JACQUES LOEB (*Pflüger's Archiv*, 1901, 88, 68—78).—The poisonous action of ions differs for various embryos and for different forms of contractile tissue. Certain other ions have an antagonistic action. The antitoxic action is confined to cations, and in this relation valency is a factor of importance. The poisonous action of a univalent cation can be neutralised by minimal quantities of a bivalent, and probably still smaller quantities of a tervalent, cation. The toxic action of a bivalent cation can be neutralised by a small quantity of another bivalent, or a relatively larger quantity of a univalent cation.

W. D. H.

**Natural Immunity against Alkaloids.** By ALEXANDER ELLINGER (*Zeit. Biol.*, 1901, 42, 228—241).—It is well known that certain animals are not affected by poisonous alkaloids. The rabbit in relation to atropine is one of the best known examples. Calmette has, however, shown that if 2 milligrams of atropine sulphate are injected directly into the brain of a rabbit, it dies in a few hours; yet it is unaffected by 0.2 gram injected into its blood. He believes the leucocytes of

this animal have the power of combining with the alkaloid and so protecting the animal. It is now pointed out that this theory is not supported by analyses of leucocytes, plasma, and brain, and that there is a want of certain control experiments. Attempts to show that the leucocytes contain more atropine than the plasma were not successful, although it is admitted that the methods of estimation of minute quantities of the alkaloid are not at present very accurate. W. D. H.

**Protective Substances of Immune Sera.** By E. W. AINLEY WALKER (*J. Hygiene*, 1902, 2, 85—100).—From experiments with *Bacillus typhosus*, conclusions are reached which differ somewhat from Ehrlich's, especially in relation to the part played by the 'addiment.' The amount of the 'immune substance' needed for protection against  $n$  minimum lethal doses of a bacterium is contained in  $(nd - e)/(d - e)$  c.c. of its immune serum, where  $d$  is the minimum lethal dose, and  $e$  the largest dose, invariably not fatal, and the serum equivalent of one minimum lethal dose. The addiment is a leucocytic ferment which is not extremely special to the species, and is increased during and by immunisation. Agglutinins assist the phagocytic process of ingestion. W. D. H.

**Immune Substances.** By ERNST P. PICK (*Beitr. chem. Physiol. Path.*, 1901, 1, 351—444).—This is an attempt to isolate various 'immune substances' of the antitoxic blood in various diseases. They are associated with the globulin of the serum, usually with the euglobulin fraction. The property of preventing the action of 'coagulins' is also possessed by euglobulin, whilst antirennin action is a property of pseudo-globulin. Calcium salts and phosphates have no influence on the former action. W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Nitrogen-assimilating Bacteria in Soils.** By P. NEUMANN (*Landw. Versuchs-Stat.*, 1901, 56, 203—206).—Extracts of the above-ground portions of *Vicia faba*, of the roots (both previously extracted by heating with water for 24 hours on a water-bath), and of peaty soil were inoculated with an extract of bean roots, of the nodules, and of the adhering soil, as well as with the crushed roots and nodules themselves, and with an extract of the stems and leaves. Assimilation took place in each case during the two weeks which the experiments lasted, and the effect of the three methods of inoculation was very similar. The greatest assimilation took place in the extract of stems and leaves, whilst in peat extract it was very much more restricted. Assimilation depends, therefore, essentially on the organic food at the disposal of the microbes.

The same minerals were added to all the cultivations.

N. H. J. M.

**Process for Inoculation with Soil Bacteria.** By FR. BAYER & Co. (*Bied. Centr.*, 1902, 31, 12—14; from *Bl. Zuckerrübenbau*, 1901, 217).—A new bacillus, described as "Alinit-Bacillus Beta," to distinguish it from the ordinary alinit bacillus (Alpha) is described, which is obtained from humous soils which have responded to the application of alinit. Such soils are found to contain considerable amounts of furfuroids.

It was found that in every soil on which increased yields of cereals were obtained after applying alinit, the original alinit bacillus was accompanied by the new bacillus. The latter does not alone assimilate free nitrogen, but it increases the assimilating power of ordinary alinit.

The simultaneous action of the two bacilli was found to benefit, not only cereals, but all other crops.

It is desirable to add to the soil a certain amount of carbohydrate (solution of molasses, for instance) when employing alinit.

N. H. J. M.

**Alcoholic Fermentation of the Must of Indian Figs.** By C. ULPANI and L. SARCOLI (*Gazzetta*, 1901, 31, ii, 395—413).—The authors have studied the alcoholic fermentation of the must of the Indian fig which is largely grown in the southern parts of Italy, with a view to the commercial production of alcohol. The juice expressed from the crude fig pulp is found to contain 12·8 per cent of sugar. When left to itself, the must undergoes spontaneous fermentation by means of a special organism to which the name *Saccharomyces Opuntiae* is given. The authors have studied the morphological and biological characters of this yeast, which does not liquefy gelatin or starch paste, has no action on sucrose or maltose, and produces no pigment of any kind. It ferments dextrose and laevulose, but exerts no action on lactose, raffinose, galactose, mannitol, or dulcitol. Comparative experiments have been carried out on the fermentation of sterilised Indian fig must by means of *Saccharomyces Pastorianus II.* and *S. Opuntiae*, the results being shown briefly in the following table, all the numbers representing grams.

	Sugar in must.	Alcohol (calc.).	Alcohol (found).	CO <sub>2</sub> (calc.).	CO <sub>2</sub> (found).	Sugar remaining.
<i>S. Opunt.</i> .....	19·8	10·12	5·62	9·6800	5·4664	0·9500
<i>S. Past. II.</i> .....	19·8	10·12	8·21	9·6800	10·3992	traces

It will thus be seen that *S. Pastorianus II.* gives a yield of alcohol which nearly approaches the theoretical amount and far exceeds the quantity obtained with *S. Opuntiae*. The spontaneous fermentation of the must of the Indian fig is thus badly adapted for the production of alcohol and the authors find that if the unsterilised must is inoculated with *S. Pastorianus II.*, the latter organism is very quickly checked by spontaneous inoculation and growth of *S. Opuntiae*. The investigations

are being continued in the hope of discovering a yeast which will not be checked by *S. Opuntiae* and will yield a large proportion of alcohol.

T. H. P.

[Yeast Trypsin.] By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1901, 34, 158—161).—Polemical. A reply to Kutscher (*Abstr.*, 1901, ii, 523).

W. D. H.

**Physiological Action of Formaldehyde.** By WALDEMAR KOCH (*Amer. J. Physiol.*, 1902, 6, 325—329).—Experiments on yeast lead to the conclusion that formaldehyde does not act by the formation of active oxygen or by destroying the zymase, but brings about the death of the cell indirectly by rendering its proteid food supply useless, and by preventing the digestion of proteids always going on within the body of the cell. Similarly, the conclusion is drawn in connection with experiments in pancreatic digestion that the enzyme is not directly affected by formaldehyde. The harmful action is on the proteid substances on which trypsin acts, these being rendered indigestible by the formaldehyde, in proportion to its strength and the time of exposure.

W. D. H.

**Chlorophyllous Assimilation.** By M. HARROY (*Compt. rend.*, 1901, 133, 890—891. Compare Friedel, *Abstr.*, 1901, ii, 411).—The chlorophyll contained in extract of spinach has no action on carbon dioxide in direct sunlight; the assimilation does not appear to take place outside the living organism.

G. T. M.

**The Proteolytic Enzyme of Nepenthes.** By SIDNEY H. VINES (*Ann. Bot.*, 1901, 60, 563—573).—Although in the main the conclusions of Clautriau on the digestive process in pitcher plants are confirmed, one of them is disputed. Clautriau believes that nepenthin most nearly resembles pepsin in its action. It is admitted that nepenthin is most active in acid media, nevertheless tryptophan occurs in the digestive products; this is regarded as the most distinguishing characteristic of tryptic digestion. Tryptic digestion appears to be the more primitive form of the digestive process.

W. D. H.

**Variations in the Organic Matter during Germination.** By GUSTAVE ANDRÉ (*Compt. rend.*, 1901, 133, 1229—1231).—The cotyledons lose fat whilst the seedlings acquire fat, probably in part by the transformation of carbohydrates. The carbohydrates soluble in alcohol disappear very quickly at first from the cotyledons, but not afterwards, whilst no regular increase takes place in the plants. The cotyledons also lose the saccharifiable carbohydrates, at first very rapidly, but afterwards more slowly; simultaneously there is a gain in the plants. Cellulose probably takes no part in feeding the young plant. Vasculose increases rapidly in the plant, and the amount produced is relatively greater than the amounts of saccharifiable carbohydrates and cellulose. The total nitrogen decreases in the cotyledons, and migrates to the plants.

N. H. J. M.

**Can Leucine and Tyrosine serve as Nutrients for Plants?** By ERNST SCHULZE (*Landw. Versuchs-Stat.*, 1901, 56, 97—106).—After referring to negative results obtained by Lutz (*Ann. Science Nat.*, 1899, [vii],

*Bot.*, 7, 1—103), attention is drawn to the fact that both leucine and tyrosine seem to disappear during growth (*Zeit. physiol. Chem.*, 24, and 30; and Shibata, *J. Coll. Science Imp. Univ. Tokio*, 1900, 13, Part 3). The conclusion is drawn that both substances are assimilated by phanerogams. Loew and Bokorny (*J. pr. Chem.*, 1887, [ii], 36, 279) have shown that algæ utilise leucine. N. H. J. M.

**Blue Coloration of certain Mushrooms.** By GABRIEL BERTRAND (*Compt. rend.*, 1901, 133, 1233—1236).—When certain mushrooms of the genus *Boletus* are broken, their tissues rapidly acquire a blue colour which disappears in a few minutes (Schönbein, *Phil. Mag.*, 1856 [iv], 11, 137; Bertrand and Bourquelot, *Compt. rend. Soc. Biol.*, 1895 [x], 2, 579—582).

The chromogen, *boletol*, which the author has now isolated has the character of an acid phenol. Solutions of boletol in pure water show the blue coloration only with difficulty when treated with laccase, but the coloration is readily obtained in solutions of potassium boletate or by adding to boletol an alkali or alkaline earth metal. In absence of sufficient quantity of such a metal, there is a tendency for a reddish coloration to be produced.

The substances necessary to produce the blue colour are therefore oxygen and boletol, laccase and manganese, and an alkali or alkaline earth metal. N. H. J. M.

**Reserve Carbohydrates of the Seed of *Aucuba Japonica*, L.** By G. CHAMPENOIS (*Compt. rend.*, 1901, 133, 885—887).—The seed of *Aucuba Japonica*, L., contains both soluble and insoluble carbohydrates. The soluble portion extracted by boiling alcohol was found to contain sucrose and a glucoside. The insoluble residue contains a galactan, mannan, and pentan, giving, on hydrolysis, galactose, mannose, and a pentose respectively. The pentose appears to be arabinose.

G. T. M.

**Supposed Presence of Solanin in Tobacco Seeds.** By JOHANNES STARKE (*Bull. Acad. Roy. Belg.*, 1901, 7, 379—383. Compare Abstr., 1900, ii, 234).—The seeds of *Nicotiana macrophylla* and *Tabac de Gramont* do not contain solanin. H. R. LE S.

**Dried Brewers' Grains.** By TH. DIETRICH (*Landw. Versuchs-Stat.*, 1901, 56, 207—256).—A detailed account of the processes involved in the production of brewers' grains, with the results of analyses by various investigators. N. H. J. M.

**Dried Distillery Grains.** By TH. DIETRICH (*Landw. Versuchs-Stat.*, 1901, 56, 257—262).—The grains are obtained in the so-called aëration-process in the preparation of yeast. The only published analyses seem to be those given by Wolff (Menzel and von Lengerke's *Landw. Kalender*, 1890).

The results of analyses now given show that the crude proteid contains 95 per cent. of pure proteids. The digestibility resembles that of brewers' grains. The amount of fat varies a good deal and increases with the amount of maize employed.

The dried grains resemble brewers' grains as regards their use in cattle feeding, but they generally have a higher value than the latter.

N. H. J. M.

**Influence of Nutritive Salts on the Production of Nodules on [the Roots of] Peas.** By EM. MARCHAL (*Compt. rend.*, 1901, 133, 1032—1033).—Water-culture experiments, in which peas, inoculated from young nodules, were grown in dilute solutions of various salts. It was found that alkali nitrates in 0.01 per cent. solutions, ammonium salts in 0.05 per cent., potassium salts in 0.5 per cent., and sodium salts in 0.3 per cent. solutions prevented the formation of nodules. Calcium and magnesium salts, on the other hand, are favourable, and phosphoric acid, although its action varies according to the base, seems also to have a stimulating effect. N. H. J. M.

**[Effect of Manures on] the Development of Leguminous Root Nodules.** By ÉMILE LAURENT (*Compt. rend.*, 1901, 133, 1241—1243).—In the case of peas, it was found that ammonium sulphate reduced the number of nodules the first year, whilst potassium salts and superphosphate both promoted their formation. Calcium carbonate reduced the number, but increased the size of the nodules. With sodium chloride, the nodules were small and the number was diminished. In subsequent years, the effects of the manures became more pronounced, the nodules disappearing altogether in the plots which received sodium nitrate and ammonium sulphate, and becoming more and more numerous on the plots which had potassium salts and superphosphate. The soil, however, in which the peas (under the influence of nitrogenous manures) grew without nodules, was found to contain the microbes and was successfully employed for inoculation.

The results obtained with peas do not hold good for all leguminous plants. In the case of beans, for instance, nitrogenous manures were found to promote the formation of nodules. Hairy vetches manured with sodium chloride had many nodules. N. H. J. M.

**Cultivation of Clover on Soils without Calcium Carbonate.** By PIERRE P. DEHÉRAIN and E. DEMOUSSY (*Compt. rend.*, 1901, 133, 1174—1177).—Clover was grown in heath soil manured with potassium phosphate, and in the same soil with (1) 20 per cent. of calcium carbonate, (2) 10 per cent. of garden soil, and (3) both calcium carbonate and garden soil in the same quantities as before. The original soil contained about 1 per cent. of calcium as sulphate.

The results showed that the original soil contains the nodule bacteria and that the yield of clover was greatly increased by the addition of garden soil. Calcium carbonate had very little effect when applied alone, and diminished the yield when added along with garden soil, as compared with the yield obtained under the influence of garden soil alone.

Further experiments with a soil from Brittany, which contained no calcium at all, showed that it was greatly benefited (for clover) by adding 10 per cent. of calcium carbonate, whilst garden soil had much less effect.

N. H. J. M.

**Nutrition and Physiological Studies on Hops.** By THEODOR REMY and O. ENGLISCH (*Bied. Centr.*, 1901, 30, 808—810; from *Bl. Gersten-, Hopfen-, u. Kartoffelbau.*, 1900, 457).—The maximum growth of hops was found to be during the period of flower and fruit production. In the spring, the perennial portions of the plants contain 30—40 per cent. of the total nitrogen, potassium, and phosphoric acid required. Assimilation from the soil is at first slow, but afterwards increases, and reaches a maximum when the fruit develops; when the hops are ripe, assimilation ceases. The taking up of calcium and magnesium follows on the whole that of the constituents already mentioned, but the supply of these constituents in the root is less than that of nitrogen, potassium, and phosphoric acid, and their assimilation seems to continue after the ripening period.

As regards the total amounts of minerals, the hop plant requires very considerable amounts of calcium and magnesium, more even than red clover. Large amounts of potassium are also required.

Nitrogen, potassium, and phosphoric acid migrate from the stems and leaves, before their death, to the fruit; but there is simultaneously a gain of calcium and magnesium in the leaves. The roots also acquire more nitrogen, potassium, and phosphoric acid.

N. H. J. M.

**Partial Milking.** By EDWIN ACKERMANN (*Chem. Zeit.*, 1901, 25, 1160—1162).—A paper containing several tables and illustrated with curves showing the increase of fat as the milking proceeds.

The idea that in the ordinary process of milking the fat keeps on regularly increasing is not correct, except in the case of goats. Every teat yields a milk which shows a constantly increasing percentage of fat. If, as is customary, two teats are emptied first, the same phenomenon will again present itself when emptying the other pair, as the milk will be again poor in fat at first. The minimum, and also the maximum, amount of fat slightly increases for the milk removed by each succeeding teat.

L. DE K.

**Production of Milk and Butter: Effect of Feeding on the amount of Fat in Milk.** By L. MALPEAUX and E. DOREZ (*Ann. Agron.*, 1901, 27, 561—593).—Of the various rations employed with nutritive ratios of 1:8 to 1:3, the best results were obtained when the ratio was 1:6. More concentrated foods increase the live weight at the expense of milk and butter production.

The comparison of the different cakes used for feeding showed that cotton cake was the best, then followed cocoa-nut, linseed, sesamé, colza, and poppy-seed cakes. Mangel leaves, maize fodder, and mustard are unsuitable for butter production, and should only be used in limited quantities. Potatoes are not recommended; carrots are better than mangels, but not in proportion to their cost. Oats increase butter production, and wheat bran promotes milk secretion but should not be used so as to exclude cake.

N. H. J. M.

**Utilisation of Gluten Proteid by Ruminants.** By OSCAR KELLNER (*Landw. Versuchs-Stat.*, 1901, 56, 149—152).—It was found



that extracting gluten meal prepared from wheat with ether for 16 hours did not remove the whole of the fat, and that a further considerable amount of fat could be extracted after digestion with pepsin and hydrochloric acid. This involves a correction in the results as previously given (*Landw. Versuchs-Stat.*, 1894, 44, 390), but does not affect any of the conclusions drawn from them. N. H. J. M.

**Causes of Sterility in Peat Soils.** By J. DUMONT (*Compt. rend.*, 1901, 133, 1243—1246).—Whilst the nitrogen present in a sample of peaty soil nitrified extremely slowly, it was found that ammonium sulphate added to the same soil was quickly nitrified, indicating that the soil is favourable to nitrification, but not to the production of ammonia from organic nitrogen. Further experiments showed that the different samples of peaty soil examined contained very little potassium, and that the addition of potassium carbonate to one of them gave rise to the production of ammonia. The best results were obtained by adding 2 per cent. of potassium carbonate, but 1 per cent. had a very considerable effect. The conclusion is drawn that potassium carbonate ought to be applied to peat land. N. H. J. M.

**Green Manuring on Heavy Soil.** By F. HANUSCH (*Bied. Centr.*, 1902, 31, 11—12; from *Zeit. Landw. Versuchswes. Oesterr.*, 1901, 772).—Plot experiments of 5—8 ares are described in which the produce of various crops, and also their nitrogen and ash content, both in the portions above ground and in the roots, were determined. The amounts of nitrogen and of organic matter per hectare were as follows: field peas, 18.6 and 378.1; horse beans, 41.4 and 887.1; vetches, 75.5 and 1543.6; and white mustard, 90 and 3067.4 kilos. The most remunerative crop was therefore white mustard, and this was followed by vetches, horse beans, and field peas in the order given. The crops have been used as manure for a cereal. N. H. J. M.

**Relative Value of different Phosphates.** By DIMITRY PRIANISCHNIKOFF (*Landw. Versuchs-Stat.*, 1901, 56, 107—140).—The results of sand culture experiments showed that the availability of sparingly soluble phosphates varies with different crops. It will be possible when more data are obtained to exactly express the coefficient of availability in the case of different plants. The following numbers indicate provisionally the relative amounts of phosphoric acid assimilated in sand culture experiments:

	Phosphorite.	Bone meal.	Basic slag.	CaHPO <sub>4</sub> .
Cereals.....	0—10	40	60—70	100
Buckwheat, lupins, &c. ...	60	90	100	100

Phosphorite should not be applied to black soil or to light soils (probably not to any soils long cultivated) for cereals, but only for buckwheat, mustard, lupins, and peas. In the case of peat land, however, and acid soils generally, phosphorite may be applied for any crop. An experiment on black soil is recorded in which, without manure, buckwheat gave much more produce than wheat: the addition of phosphorite and of sodium dihydrogen phosphate greatly increased the yield of

wheat, but not the yield of buckwheat. This is attributed to the greater assimilative power of buckwheat for sparingly soluble phosphoric acid.

Experiments are described in which phosphates were applied in conjunction with varying amounts of ammonium sulphate, and of sodium, calcium and ammonium nitrates. It was found that ammonium salts act as a strong solvent for phosphorite. N. H. J. M.

**Action of Kainite and of High Per Cent. Potassium Salts.** By MAX GERLACH (*Bied. Centr.*, 1901, 30, 794—795; from *Fühling's landw. Zeit.*, 1901, 11 and 12).—Experiments with barley in soil poor in potassium showed that kainite produced far better results than high per cent. "potassium salts" containing the same amount of potassium. This is attributed to the fact that the kainite contained twice as much sodium chloride as the "potassium salts"; and the conclusion is drawn, in agreement with Wagner, that sodium can economise potassium partly by liberating potassium from the soil and partly by satisfying the mineral requirements of the crop.

In the case of potatoes, "potassium salts" have the advantage; as compared with kainite, that they contain less chlorides; but even "potassium salts" reduce the percentage of starch. N. H. J. M.

**Manurial Value of the Excretions of Cows.** By W. S. SWEESTER (*Bied. Centr.*, 1901, 30, 793—794; from *Pennsylvania State Coll. Agric. Exper. Stat. Bull.*, 54, 1900).—The results of analyses of the milk, fæces, and urine of two cows fed, during 5 periods, with known amounts of different foods, showed that the milk contained about one-sixth of the total nitrogen, one-quarter of the phosphoric acid, and a tenth of the potash contained in the whole of the excretion.

N. H. J. M.

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### Analytical Chemistry.

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**New Drying Oven.** By HERMANN THOMS (*Ber.*, 1901, 34, 4254—4255).—The chief novelty in the drying oven described is that it has holders for the stems of funnels instead of the usual holes in a shelf.  
R. H. P.

**Estimation of Fluorine in Fluorides easily Decomposable by Sulphuric Acid.** By W. E. BURK (*J. Amer. Chem. Soc.*, 1901, 23, 825—829).—A modification of Carnot's process (*Abstr.*, 1892, ii, 911). The apparatus consists of a 150 c.c. Erlenmeyer flask closed with a trebly perforated rubber stopper. The first hole admits a rectangularly bent tube reaching to nearly the bottom of the flask, the other end being connected with two straight drying tubes containing respectively dry calcium chloride and glass wool moistened with sulphuric acid. The second and third holes are closed with a

stopcock funnel and a bent glass tube, one end of the latter terminating just below the rubber stopper, whilst the other end projects into a U-tube plugged below the corks with glass wool. This tube is in turn connected with two U-loops bent from 5 mm. glass tubing connected with tight rubber joints and plugged with glass wool, the plugs being designed to interrupt the air current and stop any sulphuric acid fumes not previously eliminated; these loops are immersed in beakers containing cold water. The products of the reaction are passed to the bottom of a glass cylinder containing some mercury; the cylinder is closed by means of a trebly perforated rubber stopper, through the second hole of which passes a stopcock funnel, whilst the third admits an exit tube connected with an aspirator. Before use, the whole apparatus is heated with a naked flame while a slow current of air is passed in order to secure complete dryness. When the current is stopped, 20 c.c. of a 10 per cent. solution of potassium fluoride are introduced by means of the funnel into the cylinder and the stopper of the Erlenmeyer flask having been momentarily removed, a mixture of 0.20 gram of the dried fluoride with 3 grams of pure, recently ignited silica are introduced. Forty c.c. of sulphuric acid previously aerated by a current of dry air while heated at  $165^{\circ}$  are introduced into the funnel, and the acid is now admitted into the flask and heated in an oil-bath for an hour and a half at  $120^{\circ}$ , a slow current of air being passed all the time. The liquid above the mercury, which has absorbed the silicon fluoride, is now transferred to a beaker and mixed with an equal volume of 90 per cent. alcohol. The precipitate, consisting of potassium silicofluoride, is collected on a Gooch crucible using reduced pressure, washed with alcohol, dried at  $100^{\circ}$ , and weighed. The weight multiplied by 0.34511 gives the fluorine, and this multiplied by 2.0527 equals calcium fluoride.

L. DE K.

**Colorimetric Method for Estimating Oxygen dissolved in Water.** By WILLIAM RAMSAY and IDA HOMFRAY (*J. Soc. Chem. Ind.*, 1901, 20, 1071—1074).—The process is based on the fact that an ammoniacal solution of cuprous chloride turns blue in the presence of oxygen, the intensity of the colour depending on the quantity of oxygen present. The effluent to be tested is introduced by means of a special arrangement into a modified Mill's colorimeter, contact with the air being excluded by means of a layer of paraffin oil; the comparison tube contains water saturated with air (oxygen) at a known temperature. Into both tubes are introduced the same quantity of cuprous chloride, dissolved in hydrochloric acid immediately before use, and then an excess of ammonia. After a while, the two colours are compared and the usual calculation is applied. If the effluent contains much lime, it is advisable to add to the contents of both tubes 2 or 3 c.c. of a hot saturated solution of ammonium chloride in order to prevent turbidity on adding ammonia. If the effluent is yellowish, the water used for comparison may be slightly tinged with an alkaline solution of *p*-nitrophenol. For a minute description of the process, and also for that of a portable apparatus devised by the authors, the original paper should be consulted.

L. DE K.

**Photometric Estimation of Sulphates.** By D. D. JACKSON (*J. Amer. Chem. Soc.*, 1901, 23, 799—806).—The apparatus consists of a 100 c.c. Nessler jar, 2.5 cm. in diameter and 17 cm. to the 100 c.c. mark, and graduated from the bottom in centimetres and millimetres. A standard candle is used, above which is suspended an iron ring with an indicator so that the top of the ring is always three inches above the top of the candle. The observations are made in a dark room, and the candle is placed over a dark surface. The tube intended for the solution is enveloped in a brass holder which comes up almost to the 100 c.c. mark and has a broad disc at the bottom which shields the eye from the strong light below. The bottom of this cylindrical tube is entirely open except for a very narrow rim which serves to keep the glass tube in place. The inside of the holder is painted a dull black to prevent reflection. The solution to be tested is washed into the jar and slightly acidified with hydrochloric acid. After diluting with water nearly to the mark, 2 grams of solid barium chloride are added, and the whole is diluted to exactly 100 c.c.; the tube is then closed with a pure rubber stopper, and thoroughly shaken until the barium chloride is dissolved. The tube is now placed in the brass holder and the contents are poured backwards and forwards from the tube into a lipped beaker, keeping the precipitate constantly shaken up so as to have a uniform turbidity. When the holder is placed on the iron ring suspended 3 inches above the top of the candle and the eye held quite near the top of the glass tube, a point is finally reached when the flame of the candle just disappears. The height at which the solution stands in the tube (reading at the bottom of the meniscus) is then taken, and from this reading the percentage of sulphuric anhydride may be calculated from the formula  $x = 0.0574/y + 0.1$ , in which  $x$  equals the sulphuric anhydride and  $y$  the depth in centimetres of the liquid in the cylinder. Tables are given to save calculation.

To apply the process to waters, 100 c.c. of the sample (concentrated if necessary) are used. Water poor in sulphates may also be tested by comparing the turbidity produced by barium chloride with silica standards such as are in use for the determination of the turbidity of drinking water; a standard of 10 in silica is equivalent to 1.45 parts per million of sulphuric anhydride. Of urines, it is sufficient to take 10 c.c.; for coal and cement, 1 gram will suffice.

The results are sufficiently accurate for technical purposes, as in most cases it is only a question of the presence of an undue excess of sulphur or sulphates.

L. DE K.

**Estimation of Nitrogen.** By FERDINAND JEAN (*Ann. Chim. anal.*, 1901, 6, 441).—When using conical cast iron flasks of 1 litre capacity as distillation flasks in the Kjeldahl process, it was found that a portion of the liquid was violently carried over into the worm of the condenser, and so passed into the acid in the receiver. To remedy this defect, the flasks are now fitted with a bulb of 500 c.c. capacity. The tube connected with the bottom of the bulb has a diameter of 15 mm., and passes through a cork into the distilling flask; the tube at the top

has a diameter of 18 mm., is bent laterally, and connected with the condenser. During the distillation, the liquid may fill about one-third of the bulb; to prevent too strong a condensation, the bulb and the top part of the flask are wrapped round with paper.

The use of sodium hypophosphite instead of sulphide is recommended to decompose ammoniacal mercury compounds during the distillation. L. DE K.

**Colorimetric Estimation of Nitric Acid in Water.** By HERM. NOLL (*Zeit. angew. Chem.*, 1901, 14, 1317—1319).—Twenty c.c. of sulphuric acid containing 0.05 gram of brucine are added to 10 c.c. of the sample of water; should this contain more than 0.05 gram of nitric acid per litre, it must be first suitably diluted. After a quarter of a minute's action, the liquid is poured into a Hehner's cylinder containing 70 c.c. of water. For comparison, a solution containing 0.1871 gram of potassium nitrite per litre is used, which is treated in the same manner, and of the darker-coloured liquid a portion is then withdrawn until the colours are equalised. Nitrites, if present, should be allowed for. L. DE K.

**Estimation of Nitrates in Chlorinated Waters.** By RENÉ MARCILLE (*Ann. Agron.*, 1901, 27, 596—600. Compare Abstr., 1885, 1093).—The picrate method gives incorrect results in presence of chlorides. The following modification was found to be very satisfactory. After determining the amount of chloride present, a slight excess of a 20 per cent. ammoniacal solution of silver sulphate is added to 10 c.c. of the water in a 25 c.c. porcelain basin. As a rule, only a fraction of a cubic centimetre of silver sulphate is required, and a pipette is employed which gives an ascertained number of drops for each c.c. The water is then evaporated on a sand-bath heated not much above 120°. The cold residue is treated with 1.5 to 2 c.c. of a solution of phenol (8.1) in sulphuric acid (100 parts), every particle of silver chloride being detached from the dish and well crushed. About 10 c.c. of water and a slight excess of ammonia are then added, and the whole poured into a 50 or 100 c.c. flask, which is filled with water. Filtration is unnecessary, as any undissolved silver chloride quickly settles. The comparison of the coloration is made in the usual manner. N. H. J. M.

**Gasometric Estimation of Nitrites in Urine.** By PAUL GERLINGER (*Zeit. angew. Chem.*, 1901, 14, 1250—1252).—Gailhat's process (Abstr., 1900, ii, 686) may be applied to the estimation of nitrites in urine. The method employed by the author is briefly as follows: the urine is boiled in an Erlenmeyer flask with solution of ammonium chloride, the steam being condensed and returned by a vertical condenser, and the liberated nitrogen collected over aqueous potassium hydroxide contained in an azotometer. Before adding the urine to the heated solution of ammonium chloride by means of a dropping funnel, the air of the apparatus must be completely displaced by a current of carbon dioxide, and this gas is again passed after the reaction is complete to sweep out every trace of nitrogen. The results of several experiments are communicated to show the accuracy of the method. L. DE K.

**Estimation of Phosphoric Acid in Phosphates.** By JOSEPH A. MULLER (*Bull. Soc. Chim.*, 1901, [iii], 25, 1000—1002).—For the standardisation of uranium solutions for the volumetric determination of phosphoric acid in phosphates, the author recommends the use of the crystallised salt,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , in nitric acid solution, this salt having the advantage over sodium phosphate and hydrogen sodium ammonium phosphate that it loses its water of crystallisation with much greater difficulty, and therefore allows of greater accuracy in the preparation of the solutions. Attention is also called to certain precautions to be observed in the analysis of this salt. A. F.

**Preparation of Volumetric Solution of Sodium Arsenite.** By GEORG LUNGE (*Zeit. angew. Chem.*, 1901, 14, 1293).—A reply to Petriccioli and Reuter (*ibid.*, 1181), who object to Lunge's method of preparing sodium arsenite by boiling arsenious acid with solution of sodium hydrogen carbonate, as sodium carbonate will be formed and this consumes iodine.

The authors' experiments show that a solution of sodium carbonate absorbs but minimal quantities of iodine; moreover, a solution of sodium hydrogen carbonate, after half an hour's boiling, contains no sodium carbonate, but an intermediate carbonate which scarcely acts on iodine, particularly in presence of potassium iodide. L. DE K.

**Estimation of Carbon in Steel by Direct Combustion.** By BERTRAM BLOUNT (*Analyst*, 1902, 27, 1—5).—Five grams of steel drillings or turnings are mixed with 15 to 20 grams of recently fused lead chromate and placed in a large porcelain boat, which in turn is placed in a long, deep tray of sheet platinum and the whole slid into a porcelain combustion tube. The front part of this tube containing copper oxide is heated in a Fletcher combustion furnace, and the back part also is similarly heated, but the precise spot where the boat lies is heated for one hour by means of a benzoline blast lamp. The combustion takes place in a current of purified oxygen and the products of combustion are passed through specially constructed drying and absorption apparatus. The paper is fully illustrated. L. DE K.

**Estimation of Silicon in Steel.** By GEORGE AUCHY (*J. Amer. Chem. Soc.*, 1901, 23, 817—820).—Drown's method (evaporation with nitric and sulphuric acids) gives good results with samples of pig iron, but with steels the results are much too low. This, according to Dudley, is caused by the iron sulphate enclosing and protecting the silicic acid from the dehydrating action of the sulphuric acid and may be remedied by vigorous stirring; this has been confirmed by the author, but the process then becomes too tedious for use in steel works. Dudley also suggested that if the iron salts could only be kept in solution until the silica is rendered quite insoluble, it would greatly improve matters. The author found that if nitrohydrochloric acid is used instead of nitric acid, the sulphate does not separate so readily, but the loss of silica is not prevented thereby.

The old Swedish process (evaporation with sulphuric acid only) gives very satisfactory results and may be generally recommended. Both this and Drown's process give, with high silicon pig, results

which are from 0.1—0.15 per cent. too low; this loss is not due to the protecting action of iron sulphate, but to the same causes which leave a considerable amount of silica in solution in an ordinary silicate analysis after one evaporation. L. DE K.

**Analysis of Silicates.** By LEHMANN and STROHÉ (*Chem. Zeit.*, 1901, 25, 1031—1032).—To obtain a correct estimation of iron, the permanganate process should be used, after reducing the sulphuric acid solution of the ferric and aluminium oxides with zinc twisted round with platinum wire.

The following process is given by Strohé for the estimation of potassium in clays if sodium is supposed to be absent. Five grams of the sample are heated with 6 c.c. of sulphuric and 30 c.c. of hydrofluoric acid. The dry residue is dissolved in boiling water with addition of a little hydrochloric acid, and when cold diluted to 500 c.c. One hundred c.c. of the solution are first precipitated with ammonia; in the filtrate, the calcium is precipitated with ammonium oxalate, and the solution is then evaporated to dryness. After heating to expel ammonium compounds, the residue is converted into a mixture of magnesium and potassium sulphates by evaporating with sulphuric acid, and the sulphates are gently ignited and weighed. The magnesium sulphate is then estimated in the usual manner and the potassium sulphate found by difference. L. DE K.

**Estimation of Potassium by Picric Acid.** By C. REICHARD (*Chem. Zeit.*, 1901, 25, 1151—1154. Compare *Abstr.*, 1901, ii, 577).—The author has successfully estimated potassium in potassium nitrate as follows: about 0.25 gram of the nitrate is put into a weighed, glazed, spherical, porcelain dish and dissolved in just sufficient cold water; 0.7 gram of sodium picrate is also dissolved in the smallest possible quantity of cold water, both solutions are heated to boiling, and the picrate is poured into the dish. After a few hours, when the potassium picrate has almost completely crystallised, the liquid is, if necessary, poured on to a small filter, and the crop of crystals carefully washed, without being broken up, with a few c.c. of water at a time. The basin is then dried at 80° until the weight is constant. Any particles of the salt which have got on to the filter may easily be brushed off from the dry paper. The salt is soluble in water to the extent of 1 in 200, but as it contains only one-seventh part of its weight of potassium the error caused by the solubility is small. L. DE K.

**Estimation of Alkalis in Portland Cement and Natural Cements.** By THOS. B. STILLMAN (*Chem. Centr.*, 1901, ii, 1369; from *Steven's Institute Indicator*).—The filtrate from the calcium precipitate is evaporated with sulphuric acid, the residue ignited until constant in weight, and the magnesium then estimated as usual, and calculated into sulphate. The alkali sulphate is found by difference. L. DE K.

**Estimation of Cæsium and Rubidium as Hydrogen Sulphates, and of Potassium and Sodium as Pyrosulphates.** By PHILIP E. BROWNING (*Zeit. anorg. Chem.*, 1901, 29, 140—144).—Salts of cæsium and rubidium with volatile acids, when treated with



sulphuric acid and heated at between  $250^{\circ}$  and  $270^{\circ}$  until constant in weight give the acid salts  $\text{CsHSO}_4$  and  $\text{RbHSO}_4$ . On igniting over a free flame, the normal sulphates,  $\text{Cs}_2\text{SO}_4$  and  $\text{Rb}_2\text{SO}_4$ , are produced. Cæsium hydrogen sulphate shows a slight tendency to retain a little sulphuric acid.

Potassium and sodium salts, when treated with sulphuric acid and heated at  $250$ — $270^{\circ}$ , give the pyrosulphates  $\text{K}_2\text{S}_2\text{O}_7$  and  $\text{Na}_2\text{S}_2\text{O}_7$ . Under similar conditions, lithium gives neither a hydrogen sulphate nor a pyrosulphate.

J. McC.

**Standardisation of Potassium Permanganate with Iron.** By HERMANN THIELE and HANS DECKERT (*Zeit. angew. Chem.*, 1901, 14, 1233—1234).—The authors have made a series of experiments from which it appears that for the standardising of permanganate it is better to use pure oxalic acid than the various kinds of so-called pure iron recommended for that purpose.

L. DE K.

**Simple Method for the Estimation of Iron in Metabolism Experiments.** By ALBERT NEUMANN (*Chem. Centr.*, 1901, ii, 1369—1370; from *Arch. Anat. Phys.* [His-Engelmann], *Physiol. Abt.*, 1901, 541—543).—The material is completely oxidised with a mixture of sulphuric and nitric acids. The solution is rendered alkaline with ammonia, and then slightly acidified with dilute sulphuric acid. A slight excess of zinc oxide is added, the precipitate is washed by decantation, then suspended in 30 c.c. of water, and dissolved in the smallest possible quantity of hydrochloric acid; ammonia is added until a precipitate of zinc hydroxide begins to form, which is then redissolved in a little hydrochloric acid. To the liquid are now added 1—2 grams of potassium iodide and a little zinc iodide starch solution, and the iodine liberated by the ferric oxide is titrated with  $N/100$  sodium thiosulphate.

L. DE K.

**Estimation of Tungsten in Tungsten Steel.** By RUDOLF FIEBER (*Chem. Zeit.*, 1901, 25, 1083).—A modification of Fresenius's method. Five grams of steel borings are dissolved in hydrochloric acid. After boiling, the insoluble matter is collected and fused with potassium sodium carbonate, the fused mass dissolved in water, and the solution added to the main filtrate; the whole is then evaporated to dryness in a porcelain dish, and the residue heated to  $120^{\circ}$ . The mass is then dissolved in hydrochloric acid and boiled in a beaker for 3 hours, when some water is added to prevent destruction of the filter paper. The precipitated tungstic acid carries down the silicic acid and also traces of iron and chromium, and the filtrate is again boiled for 3 hours to recover the last traces of tungstic acid. The washed precipitate is ignited, fused with potassium sodium carbonate, and the fused mass dissolved in water. The filtrate is neutralised with nitric acid, boiled to expel carbon dioxide, and after ascertaining that the liquid is really neutral (easily recognisable by the yellowish-green colour of the solution), the tungstic acid is precipitated by means of mercurous nitrate; the mercurous tungstate on ignition yields tungstic acid, which can be freed from any silicic acid by evaporating with hydrofluoric acid.

L. DE K.

**Estimation of Tin by Lenssen's Method.** By JOSEPH A. MULLER (*Bull. Soc. Chim.*, 1901, [iii], 25, 1002—1004).—The author has tested the method of estimating tin volumetrically by means of iodine, and finds that, in general, even when all precautions are taken to avoid the oxidation of the stannous solutions, the figures obtained are too low. The specimen of tin employed was found by gravimetric analysis to contain 99·76 per cent. of tin, and the numbers obtained by the volumetric method varied from 98·68 to 99·35 per cent. On using pure tin, the numbers obtained were 99·31 and 99·24 per cent.

A. F.

**Analysis of Tin Ores.** By JOSEPH A. MULLER (*Bull. Soc. Chim.*, 1901, [iii], 25, 1004—1007).—For the determination of tin in tinstone, the author points out that if tin dioxide is the only reducible substance present, the loss of weight on reduction in a current of hydrogen enables the amount of tin contained in the ore to be calculated directly. It is also shown that when the ore is exposed to a medium red heat in a current of hydrogen, complete reduction is effected in 3 hours. When other reducible substances (zinc blende, galena, tungsten, &c.) are present in the ore, these must first be got rid of by treatment with various reagents.

The above method was also applied to the estimation of tin in its sulphur ores, the stannic sulphide being first converted into dioxide by calcination and treatment with nitric acid. Thus, in one case, the amount of tin found by this method was 26·77 per cent., whereas a complete analysis showed the presence of 24·94 per cent. A. F.

**Volumetric Estimation of Antimony in Hydrochloric Acid Solution with Permanganate and its Practical Application.** By O. PETRICCIOLI and MAX REUTER (*Zeit. angew. Chem.*, 1901, 14, 1179—1183).—0·5 to 5 grams of the finely powdered ore are put into a beaker and 50 c.c. of hot water and 50 c.c. of hydrochloric acid are added. After heating at 70° on a sand-bath for half an hour or an hour, the antimony will be dissolved. The solution is filtered, and the insoluble matter washed first with acidified water, then with plain water. After adding some tartaric acid, the solution is diluted to about 750 c.c., heated to 60—70°, and precipitated with hydrogen sulphide; the precipitate is washed, then rinsed back into the beaker with hot water and heated with 50 c.c. of hydrochloric acid until no more hydrogen sulphide is evolved. Water is added until a slight turbidity is formed which is then removed by adding a few drops of acid. The solution may now be at once titrated with potassium permanganate, 2 mols. of which correspond with 5 atoms of antimony. Ores or products containing the higher oxide of antimony cannot be tested in this manner, but they may be rendered soluble by fusion with sodium carbonate and sulphur. The fused mass is dissolved in water and precipitated with acetic acid; the precipitate consisting of antimony sulphide with much free sulphur is treated with potassium chlorate and hydrochloric acid, filtered, the solution again precipitated with hydrogen sulphide and treated as previously directed.

L. DE K.

**Estimation of Organic Matters in Drinking Water.** By GUSTAVE DE RIDDER (*Rev. intern. Falsific.*, 1901, 14, 149).—The author recommends the Schulze-Frommsdorff process, as this is not interfered with by the presence of chlorides. This process consists in boiling the water with  $N/100$  alkaline permanganate for 10 minutes; when cooled to  $60^{\circ}$ , the liquid is acidified with dilute sulphuric acid,  $N/100$  oxalic acid equal to the permanganate employed is added, and the excess of oxalic acid is then again titrated with permanganate. L. DE K.

**Estimation of Fused Oil in Alcoholic Liquids.** By ERNST BECKMANN (*Zeit. Nahr.-Genussm.*, 1901, 4, 1059—1064).—The author has modified his process (Abstr., 1900, ii, 175) as this did not always work satisfactorily.

To remove the fusel oil from the alcoholic liquid, 20 grams of dry calcium chloride are dissolved in 50 c.c. of the sample (brandy), and water is added to reduce the alcoholic strength to 50 per cent.; the mixture is now shaken for 10 minutes with 30 c.c. of carbon tetrachloride, and for this purpose Recklinghausen's shaking machine is recommended (Abstr., 1897, ii, 19). After transferring the carbon tetrachloride to another separating funnel containing 20—25 c.c. of water, the liquid is again shaken for 10 minutes with 20 c.c. of carbon tetrachloride and then twice in succession with 20 c.c. for 15 minutes each time; all the extracts are mixed and shaken for 5 minutes with water which removes ethyl alcohol, but as it may also remove some of the higher alcohols, these must be recovered by adding 10 grams of calcium chloride and shaking for 5 minutes with 80 c.c. of carbon tetrachloride.

To convert the amyl alcohol into amyl nitrite, the dried solution may be treated with nitrous acid evolved from arsenious acid and nitric acid, but the following modification is more convenient in practice.

The solution containing the fusel oil is dried by means of a little calcium chloride and filtered through glass wool. Three grams of powdered sodium hydrogen sulphate and 3 grams of sodium nitrite are added, and after half an hour's action the liquid is again filtered and freed from excess of acid by shaking with 3 grams of powdered sodium hydrogen carbonate; water is now added to dissolve the soda, which is then removed from the funnel. To estimate the amount of amyl nitrite, the solution is shaken with 10 c.c. of sulphuric acid; this completely decomposes the amyl nitrite with formation of nitroso-sulphuric acid. The whole is now added to 100 c.c. of water, cooled with pieces of ice, and the nitrous acid titrated with solution of potassium permanganate (1:1000). If aldehydes are present, these may be removed by shaking the carbon tetrachloride extract with powdered sodium hydrogen sulphite, dissolving the latter in a little water and removing it from the funnel. L. DE K.

**Use of Sodium Salicylate in the Estimation of Mixtures of Terpene-alcohols and their Ethers.** By GEORGES DARZENS and P. ARMINGEAT (*Bull. Soc. Chim.*, 1901, [iii], 25, 1053—1055).—Charabot and Hébert have brought forward a method for the separ-

ation of terpene-alcohols from their esters, based on the solubility of the alcohols in a 50 per cent. solution of sodium salicylate. It is pointed out that the terpene esters are capable of dissolving in 50 per cent. sodium salicylate when the latter already contains terpene-alcohols, and this may form a serious source of error in the separation of the alcohols and esters by this method.

T. M. L.

**The Copper Test for Sugar [in Urine].** By ALBERT B. LYONS (*Pharm. Rev.*, 1901, 19, 531—533).—In doubtful cases, the author operates as follows:—Two or three drops of Fehling's solution are diluted with 30 minims of water, heated to boiling, and mixed with 5 drops of the urine. After boiling for 1 minute, the contents are examined; if there should be no precipitate of cuprous oxide, this does not prove that there has not been any reduction; the liquid is therefore slightly acidified with hydrochloric acid and mixed with a few drops of a 5 per cent. solution of potassium iodide. If this should yield an abundant precipitate of cuprous iodide, sugar is present in some quantity. The experiment is now repeated, using only 1 drop of urine, and if the potassium iodide still produces a distinct cloudiness, there must be at least 1 grain of sugar per ounce of urine; urines containing more sugar must be suitably diluted.

The author confirms the amount of sugar by the picric acid test. Two c.c. of the sample are mixed with 1 c.c. of a saturated solution of picric acid and 1 c.c. of aqueous potash U.S.P., and boiled for 1 minute. The dark-coloured liquid is now diluted until it corresponds in colour with a solution made by dissolving 5 grams of potassium dichromate in a mixture of 50 c.c. of water and 25 c.c. of 10 per cent. sulphuric acid, and subsequently diluting to 100 c.c. Twenty c.c. are then deducted from the final volume, and each c.c. in excess corresponds with 1/300 per cent. of diabetic sugar.

L. DE K.

**Gravimetric Estimation of Sugar.** By O. LAUENSTEIN (*Zeit. Nahr.-Genussm.*, 1901, 4, 1026—1027).—On account of the difficulty experienced in removing the last traces of cuprous oxide from the basin, the author now removes these by means of a wet piece of ash-free filter-paper of the size of a shilling, which is manipulated with a glass rod. After removing with the wash-bottle as much of the precipitate as possible, the paper is also brought into an asbestos tube, and the whole burnt in a current of air previous to being reduced in hydrogen.

L. DE K.

**Testing of Honey.** By ALBERT HILGER (*Zeit. Nahr.-Genussm.* 1901, 4, 1142—1143).—A preliminary communication on the composition of 24 German honeys (including 9 forest honeys), 22 foreign honeys, of which 2 are from Greece, 13 from America, 1 from Spain, 1 from Roumania, 3 from Hungary, 1 from Norway, and 1 from Slavonia: also of 8 artificial products. The analyses were restricted to the sp. gr. of the solution 1:2, water, sugar before and after inversion, cane sugar, non-saccharine substances, ash, polarisation, and free acid calculated as formic acid. The behaviour of the dextrins towards yeast was also investigated. Full particulars will shortly be communicated.

L. DE K.

**Honey Dextrin.** By ERNST BECKMANN (*Zeit. Nahr.-Genussm.*, 1901, 4, 1065—1069).—Honey-dextrin, to which some pure honeys owe their right-handed polarisation, is distinguished from other dextrans by giving but a slight precipitate with barium hydroxide in the presence of methyl alcohol. The other dextrans show, however, also enormous differences in their behaviour towards barium hydroxide or basic lead acetate in the presence of methyl alcohol. It was found that those specimens which darken most with iodine yield the most abundant precipitate. The precipitation in both cases is lessened in the presence of much sugar (dextrose).

According to Monheim the benzoyl ester of honey-dextrin is most likely a mixture of a penta- and hexa-benzoate of a disaccharoid, distinguished from the ordinary dextrin compound by its solubility in ether.

L. DE K.

**Estimation of Glycogen and Starch in Sausages and Meat.** By JOSEPH MAYRHOFER (*Zeit. Nahr.-Genussm.*, 1901, 4, 1101—1106).—Glycogen and starch may be readily separated by means of 49 per cent. alcohol, but if the mixture has been subjected to the action of alcoholic potassium hydroxide, which is the case in the analysis of meat preparations, the starch retains some of this, and gelatinises when in contact with weak alcohol. In this case, the mixture should first be treated with water and sufficient acetic acid to impart an acid reaction and then mixed with excess of 96 per cent. alcohol to reprecipitate the starch and glycogen, leaving the potassium acetate in solution. The precipitate, after being washed with alcohol, is heated at 80° with 44 per cent. alcohol, the liquid is passed through a filter, and the residue washed four times by decantation with 49 per cent. alcohol. The alcoholic solutions are evaporated to a small bulk and the glycogen reprecipitated by adding an excess of 96 per cent. alcohol.

The starch, which is now free from glycogen, is dissolved in aqueous potassium hydroxide, the solution filtered, and then treated according to the conventional method.

L. DE K.

**New Apparatus for the Estimation of Volatile Acids in Wines.** By G. SELLIER (*Ann. Chim. anal.*, 1901, 6, 451—452).—Steam is generated in a wide-necked flask containing 50—60 c.c. of distilled water and heated over a spirit lamp. The flask is closed with another elongated flask which holds the 10 c.c. of wine used for the experiment, and is fitted inside with a small glass syphon, the longer limb of which just passes through the bottom of the flask into which it is fused. On boiling the water, a current of steam passes through the syphon into the wine and carries off the volatile acids, but little condensation taking place as the flask gets sufficiently heated by the steam. When about 5 c.c. of liquid are left, the heat is withdrawn, and on cooling, the wine is syphoned into the lower flask. The top flask is washed with 2 or 3 c.c. of water, which also passes through the syphon, and the fixed acids are then estimated by titration. The volatile acids are found by subtracting the fixed from the total acidity.

L. DE K.

**The Acids of Wine and the Diminution of Acidity.** By MÖSLINGER (*Zeit. Nahr.-Genussm.*, 1901, 4, 1120—1130).—The paper

is chiefly devoted to a study of the origin of lactic acid in wines. It appears to be a product of a secondary fermentation, affecting the sugar and also the malic acid which is partially removed. The lactic acid is estimated as follows: 50 to 100 c.c. of wine are freed from volatile acids by means of a current of steam, and the residual liquid rendered neutral to litmus with solution of barium hydroxide. Five to 10 c.c. of a 10 per cent. solution of barium chloride are added and the whole evaporated to 25 c.c. After making sure that the liquid is neutral, 95 per cent. alcohol is added until the volume is about 70—80 c.c., the liquid is then diluted to exactly 100 c.c. with alcohol, and filtered through a dry filter. Eighty c.c. of the filtrate are then evaporated in a platinum dish, the residue is burnt to a black ash, and its alkalinity estimated in the usual way. One c.c. of *N* acid = 0.09 gram of lactic acid.

Another good plan is to take 50—100 c.c. of wine, remove the volatile acids, and evaporate to a thin syrup with addition of 0.2—0.4 gram of tartaric acid. The solution is then introduced into a 50 c.c. graduated measure, diluted to 5 c.c., and gradually mixed with 95 per cent. alcohol until the volume is 30 c.c., when 20 c.c. of ether are added 10 c.c. at a time. When clear, the liquid is poured off, evaporated with addition of a little water, neutralised with barium hydroxide (no barium chloride is added), and treated as previously directed  
L. DE K.

**Detection and Estimation of Oxalic Acid in Hydrogen Peroxide.** By D. A. ROCHE (*Chem. Centr.*, 1901, ii, 1279—1280; from *Mon. sci.*, [iv], 15, 11, 694. Compare Arth, Abstr., 1901, ii, 622).—The author doubts whether oxalic acid frequently occurs in commercial hydrogen peroxide. To detect it, the sample, if its acidity exceeds 5 grams of sulphuric acid per litre, is partly neutralised with ammonia, mixed with ammonium acetate, and tested with a solution of calcium sulphate or chloride. If the acidity is less, there is no need to neutralise with ammonia. The estimation is carried out as follows: A quantity of the sample containing 0.1—0.2 gram of oxalic acid is diluted to 200 c.c. and the acidity is increased or reduced to about the equivalent of 2 grams of sulphuric acid per litre by adding either acetic acid or ammonia; 2 grams of ammonium acetate are added, and the oxalic acid precipitated with calcium acetate. The calcium oxalate is then titrated, as usual, with potassium permanganate. For accurate analysis, the calcium oxalate should be purified by reprecipitation.  
L. DE K.

**Commercial Lemon Juices.** By R. SENDTNER (*Zeit. Nahr.-Genussm.*, 1901, 4, 1133—1140).—From the result of a number of analyses, it appears that genuine lemon juices should show about the following composition: sp. gr. 1.034—1.039; extract 8—10 per cent., consisting of citric acid 6—9 per cent., and mineral salts 0.3—0.5 per cent., the balance being made up of cupric reducing substances (sugar). The ash should have an alkalinity equal to 2.9—6 c.c. of *N* acid.  
L. DE K.

**Separation of Glutamic Acid and Leucine by Gaseous Hydrogen Chloride.** By ALEXANDRE ÉTARD (*Compt. rend.*, 1901, 133, 1231—1233).—Glutamic acid and leucine, when present together in solution, can be readily separated by saturating with hydrogen chloride, when the insoluble hydrochloride of the former is precipitated.

The liquid products of the hydrolysis of albumins which have been neutralised and concentrated under reduced pressure, are fractionally precipitated with methyl alcohol. The two first precipitates are dissolved in a little water and saturated with hydrogen chloride; from this solution, nearly pure leucine hydrochloride can be obtained. The later precipitates are treated in the same manner; hydrogen chloride throws down a precipitate consisting of the hydrochloride of glutamic acid, free from salts of other amino-acids.

The glutamic acid obtained thus from veal formed orthorhombic crystals, melting at  $183^{\circ}$  and having  $[\alpha]_D + 0^{\circ}57'$ . K. J. P. O.

**Jolles's Process for the Estimation of Uric Acid in Urine.** By O. MAKOWKA (*Chem. Zeit.*, 1901, 25, 1159—1160).—Jolles's process (Abstr., 1900, ii, 450) is recommended as the most complete, trustworthy, simple, and accurate method for the clinical estimation of uric acid in urines. L. DE K.

**Composition of Milk.** By H. DROOP RICHMOND (*Analyst*, 1901, 26, 310—316. Compare Abstr., 1900, ii, 696).—A record of results obtained in the laboratory of the Aylesbury Dairy Co. *Mean Composition of the Milk in 1900.* 13,798 samples were analysed, and the average composition showed that both the solids (12.57 per cent.) and the fat (3.64 per cent.) were largely in excess of the legal requirements. *Accuracy of Methods used.* In most of the analyses, the fat was estimated by the Gerber method; the results obtained by this process agree within about 0.1 per cent. with those obtained by Adams' paper process, as shown by an analysis of 78 samples in duplicate. The fat, calculated from sp. gr. and solids, also agreed very well. Experiments were also made by drying on washed, or unwashed, chrysotile (Macfarlane's process) and then extracting the fat with ether; but the process was abandoned. *Variation in Fat during delivery of the Milk.* An empirical mathematical formula is given, from which it appears that the probable difference is only about 0.11 per cent., and that a difference exceeding 0.31 per cent. must be looked on with suspicion. *Variation of Constituents of Solids-not-fat.* A table is given showing that in normal milks any deficiency in solids not fat below 9 is due to lactose, and any excess to proteids. *Relation between the Proteids and Salts of Milk.* The ash may be calculated with reasonable accuracy from the proteids, using the formula  $A = 0.36 + 0.11P$ . Casein, as it occurs in milk, may be looked on as a substituted phosphoric acid combined with a molecular proportion of calcium phosphate. In the course of this investigation, it was found that milk, when passed through a porcelain filter, not only loses its casein, but the whole of its proteids.

*Acidity of Milk.* In boiled milk, this can only be caused by acid phosphates and citrates. The acidity of the milk added to the alkalinity of the ash, gives a datum for estimating the amount of citric acid. The acidity is 16.8 c.c. of *N* alkali per litre to phenolphthalein, and this, being due to acid phosphates, is equal to  $16.8 \times 2/0.97 = 34.6$  c.c. for chemical neutrality, which is equal to  $34.6 \times 0.063/1.032 \times 10 = 0.218$  per cent. of citric acid; if to this is added the 0.046 per cent. of citric acid corresponding with the alkalinity of the ash, a total of 0.264 per cent. is obtained. As very little calcium citrate is precipitated on boiling, it may be presumed that it exists in the milk as a dibasic salt. The citrates would account for 14.4 c.c. of *N* alkali, the remainder being accounted for by the acid phosphate; this is equivalent to 0.020 per cent. of phosphoric acid being present as mono- and 0.077 per cent. as dibasic phosphate.

Contrary to the views expressed by Söldner, the author believes that one-third of the base with which casein is combined in milk is sodium and not calcium, that casein forms a molecular compound with calcium phosphate, and that the citrates are present as dibasic and not as tribasic salts; hence the disagreement between Söldner and the author as regards the proportions of mono- and dibasic phosphates.

L. DE K.

**Relation between Specific Gravity, Fat, and Solids not Fat in Milk.** By NORMAN LEONARD (*Analyst*, 1901, 26, 318—319).—A recalculation, by the method previously employed (Abstr., 1900, ii, 376), of the values of the constants  $\sigma$  and  $\phi$  in Richmond's formula  $G/D = \sigma\sigma - F\phi$  (*Analyst*, 1888, 14, 121—131), where  $D$  is the density of milk (water = 1). The formula now becomes  $G/D = 3.7758 - 0.743F$  or  $F = 0.836T - 0.221G/D$ . No practical advantage is claimed for this improved formula; in fact, the author's old formula,  $F = 0.827T - 0.212G$ , seems to be more suitable when dealing with rich milks.

L. DE K.

**Calculation of the Simultaneous Addition of Water to, and Withdrawal of Cream from, Milk.** By V. GÉNIN (*Compt. rend.*, 1901, 113, 743—745).—The method of calculation is based on the fact that the specific volume of the butter has a nearly constant relation to the other characters of milk.

N. H. J. M.

**Detection of Adulterations with Margarine by the Sesamé Oil Reaction.** By PAUL SOLTSIEN (*Chem. Centr.*, 1901, ii, 1240—1241; from *Pharm. Zeit.*, 46, 850).—Both the sugar and furfuraldehyde reactions are valuable, but the stannous chloride test is less liable to give erroneous results if properly conducted. Long contact between stannous chloride and the melted fat should be avoided, and the emulsion should be caused to separate as quickly as possible by plunging the tube in water at 60°; the mixture should not, on any account, be shaken again. As soon as the tin solution has separated, the lower part of the test-tube containing it is placed in boiling water. The reaction, however, generally takes place immediately after the separation of the two layers. The test also succeeds, although in a less degree, with the fatty acids.

L. DE K.



**Analysis of Oils.** By ALESSANDRO CUTOLO (*Rev. Intern. Falsif.*, 1901, 14, 146—148).—The author has modified the nitric acid test. One gram of colourless gelatin is heated in a test-tube with 10—15 c.c. of nitric acid of sp. gr. 1.4 for a few minutes in the water-bath; when cold, the liquid is diluted to 100 c.c. with nitric acid.

One c.c. of the reagent and 5 c.c. of the suspected oil are mixed in a test-tube and heated to boiling; after removing the source of heat and waiting for one or two minutes, the tube is cooled. The colours of both the fatty mass and the acid are then observed. The following results have been obtained:—*Almond oil*, fat white, acid colourless; *nut oil*, fat white, acid colourless; *olive oil*, fat clear yellow, acid faintly coloured; *castor oil*, fat orange-yellow, acid colourless; *sesamé oil*, fat orange, acid intensely yellow; *linseed oil*, fat orange-red, acid faintly coloured; *apricot oil*, fat red, acid faintly coloured; *cotton-seed oil*, fat reddish-brown, acid faintly coloured; *hemp-seed oil*, fat reddish-brown, acid faintly coloured; *colza oil*, fat reddish-brown, acid faintly coloured; *poppy oil*, fat brown, acid faintly coloured; *grape stone oil*, fat brown, acid faintly coloured.

Tables are also given showing the acidity and refraction of 40 samples of olive and 12 samples of cotton-seed oil.

L. DE K.

**Proportion of Liquid Fatty Acids in some Fats and Oils, and their Iodine Values.** By N. J. LANE (*J. Soc. Chem. Ind.*, 1901, 20, 1083).—Boiling light petroleum is substituted for boiling ether in the separation of lead oleates from the lead salts of the saturated fatty acids, and a large number of fats and oils have been tested by the new process. The proportion of oleic acids thus found is a trifle lower than that given by the ether method, whilst the iodine absorption is a little higher.

L. DE K.

**Detection of Vegetable Fats in Animal Fats by the Phytosteryl Acetate Test.** By A. BÖMER (*Zeit. Nahr.-Genussm.*, 1901, 4, 1070—1095. Compare this vol., i, 30).—The crude cholesterol from 100 grams of the fat, after being tested microscopically for phytosterol, is heated to boiling with 2—3 c.c. of acetic anhydride for a quarter of a minute in a dish covered with a watch-glass, and the excess of acid evaporated on the water-bath. The crude mixed acetates are then recrystallised several times from boiling absolute alcohol, and after the third and following crystallisations the melting point is carefully taken. If this exceeds 116° or 117° (corr.) the sample operated on contains an admixture of vegetable fat.

Reference must be made to the original for the large amount of detailed observations on which the method is based.

The author calls attention to the necessity of correcting the readings of the thermometers in this and other cases where only small differences in melting points are used as criteria of purity. L. DE K.

**Calculation of the Percentage of Diglycerides in Fat Mixtures containing Hydroxy-fatty Acids.** By J. FREUNDLICH (*Chem. Zeit.*, 1901, 25, 1129).—The following formula for the calculation is given:  $D = M.[1683(100 - F) - 38d]/51.612$ , in which  $d$  is

the ether number of the fat-mixture,  $F$  the percentage of total fatty acids (or in the absence of soluble acids, the *Hehner number*),  $M$  the molecular weight of the diglyceride, and  $D$  the percentage of the same. The formula may also be applied in the absence of hydroxy-fatty acids.

L. DE K.

**Analysis of Waxes; Estimation of Resin; Analysis of Fictitious Wax; Wool Wax.** By FERDINAND JEAN (*Ann. Chim. anal.*, 1901, 6, 447—451).—One gram of the sample is heated with alcohol on the water-bath until melted, the mixture shaken, and allowed to cool slowly, when the undissolved matter is collected on a tared filter, and washed with alcohol until free from acidity. After drying first in the air and then over sulphuric acid, the residue, which may consist of wax, tallow, and paraffin, or ceresin, is weighed; the loss in weight represents stearic acid and resin which have dissolved in the alcohol.

To estimate the resin, the alcoholic solution is evaporated nearly to dryness, and the residue redissolved in ether, and shaken with zinc oxide, which forms an insoluble zinc stearate, but a soluble zinc resinate. The solution is then shaken in a separating funnel with dilute hydrochloric acid, a few c.c. of light petroleum are added, and the whole is again shaken, and allowed to settle. After removing the acid layer, the ether is washed with a little water and evaporated, and the residual resin dried at 100° and weighed. To the weight obtained, a correction of 1.6 per cent. must be made.

In judging the quality of a sample by the amount of potassium hydroxide required to neutralise the acidity and saponify the esters, due regard should be paid to the amount of alkali absorbed by the resin and stearic acids, and also to that required for the saponification of the tallow; the latter may be calculated from the glycerol obtained on saponification. In the absence of true wax, tallow and paraffin may be separated by boiling with alcoholic alkali and dissolving the unsaponified paraffin in ether.

Two analyses are given of adulterated waxes, one being adulterated with rosin, stearic acid, and paraffin, and the other being composed entirely of stearic acid, rosin, tallow, and paraffin. An analysis is also given of a sample of wool wax, which much resembled yellow bees-wax in appearance. It consisted of 47 per cent. of free fatty acids, 50 per cent. of unsaponifiable fat, and 2 per cent. of neutral saponifiable fat.

L. DE K.

**Estimation of Furfuraldehyde in Pepper.** By ALBERT HILGER (*Zeit. Nahr.-Genussm.*, 1901, 4, 1141—1142).—Five grams of ground pepper are completely extracted with alcohol and ether, and then distilled with 100—150 c.c. of hydrochloric acid of 1.06 sp. gr.; more acid is gradually added, and the boiling continued until 400 c.c. of distillate are collected. During the distillation, a current of carbon dioxide is passed through the apparatus.

The distillate is cooled and slowly neutralised with aqueous sodium hydroxide, then slightly acidified with acetic acid; a current of carbon dioxide is passed, and a solution of 2 grams of phenylhydrazine hydro-

chloride and 3 grams of sodium acetate in 20 c.c. of water is added with constant stirring. The osazone is collected in an Allihn's tube and washed with 100 c.c. of water; it is then dissolved in absolute alcohol and evaporated in a platinum dish at 60—70° under reduced pressure and finally weighed.

L. DE K.

**A new Ureometer.** By LÉON FREDERICQ (*Trav. du lab. de L. Fredericq, Liège*, 1901, 6, 132—134; from *Vol. jubilaire de la Soc. de Biol.*, 1889).—A new ureometer, a modification of Yvon's, is described and figured. The discredit into which the hypobromite method of estimating urea has fallen is not entirely justifiable.

W. D. H.

**The Alkalimetric Factors of some Diacid Alkaloids.** By HARRY M. GORDIN (*Arch. Pharm.*, 1901, 239, 645—647).—Control estimations made with pure materials by the author's method (*Abstr.*, 1900, ii, 119) show that with quinine and quinidine good results are obtained, but with cinchonine and cinchonidine the results are 5 per cent. too low, the calculation being made on the assumption that the precipitate has the composition  $\text{AlK}, \text{HI}, \text{I}_n[\text{AlK} = 1 \text{ mol. alkaloid}]$ .

C. F. B.

**Characteristic Reaction of Morphine.** By GUSTAVE FLEURY (*Ann. Chim. anal.*, 1901, 6, 417—418).—A particle of the suspected alkaloid, of the size of a pin's head, is placed in the centre of a saucer and dissolved in a drop of dilute sulphuric acid (1:20). A little lead dioxide is added and the mixture stirred for 6 or 8 minutes. After waiting for another 3 or 4 minutes, the lead dioxide has deposited, and a clear drop of liquid may be obtained by inclining the dish. On adding a drop of ammonia, a brown coloration at once makes its appearance.

L. DE K.

**Detection of Indican in Urine.** By CASIMIR STRZYŻOWSKI (*Chem. Centr.*, 1901, ii, 1181—1182; from *Oesterr. Chem. Zeit.*, 4, 465—468).—Amann's process for the quantitative estimation of indican in urine (*Abstr.*, 1898, ii, 659) is untrustworthy; the statement that albumin is not precipitated by persulphates is erroneous. Graziani's process is a useful one. Two or three c.c. of a mixture of two drops of officinal solution of ferric chloride in 50 c.c. of sulphuric acid are carefully poured down the side of a test-tube containing 5—10 c.c. of urine. According to the amount of indican present, a cherry-red, violet, or blue ring will make its appearance at the place of contact.

The author has worked out another method. If the sample has a sp. gr. over 1.015, 20 c.c. are mixed with 10 c.c. of a 10 per cent. solution of lead acetate; if below 1.015, 5 c.c. of lead solution are added, and then 5 c.c. of water. Fifteen c.c. of the clear filtrate are mixed with a drop of 1 per cent. solution of potassium chlorate, then with 5 c.c. of chloroform, and finally with 15 c.c. of pure fuming hydrochloric acid. On shaking for 10—15 minutes, the maximum coloration is obtained. If the chloroform is distinctly blue, another drop of chlorate may be added, and the shaking repeated to see whether the blue colour may yet increase, but as a rule it will be found that the one drop is sufficient. From the intensity of the colour, in conjunc-

tion with other data, it is possible to judge whether indican is present in normal or in abnormal amount.

L. DE K.

**Detection of Artificial Sweetening Materials in Beer.** By A. SARTORI (*Chem. Zeit.*, 1901, 25, 953).—The author states that the test for "saccharin," dulcin, and similar sweetening materials by Morpurgo's process (acidifying with phosphoric acid and shaking with a mixture of ether and light petroleum; *Abstr.*, 1898, ii, 359) is not interfered with by the presence of sucrose, dextrose, starch-sugar, lactose, malt-extract, glycerol, mannitol, dextrin, honey, or extract of dates, figs, or liquorice, none of these passing into the ethereal solution.

L. DE K.

**Apparatus and Method for Estimating the Extractive Matter in Kiln-dried Malt.** By A. GAWALOWSKI (*Zeit. anal. Chem.*, 1901, 40, 641—643).—A usual method of estimating the extractive matter of malt is to mix 10 grams of the ground malt with 400—450 c.c. of cold water, and digest in the cold for an hour, then heat to 55° and raise the temperature at the rate of 1° per minute to 75°, at which it is maintained until a drop, tested with iodine solution, shows that all the dextrin is converted into sugar. The mixture is then boiled, cooled, and made up to 533 grams, the assumption being made that the exhausted grains amount to 33 grams, which, however, is not universally true. In the filtered wort, the amount of extractive matter is ascertained either aërometrically, or, better, by evaporation and weighing. The mashing is better conducted under a slight pressure, and, with the object of being able to remove samples for testing without impairing the pressure, an apparatus has been devised consisting of a stout glass flask of 1½ litres capacity with a screw thread in the neck so that a cork can be screwed in. The cork carries three tubes, all furnished with stopcocks. One tube descends to the bottom of the flask and serves for withdrawing samples. A second is connected with a manometer; the third, which opens just below the cork, allows the wort to be drawn off when the flask is inverted. In this flask, 100 grams of malt are mashed with 1 litre of water at the temperatures above stated: the pressure should not exceed ¾ of an atmosphere. When a sample shows the absence of dextrin, the temperature is raised to 100°. After cooling, the wort is drawn off and its contents estimated. This method requires no assumption to be made respecting the percentage of the exhausted grains, and obviates the troublesome washing out of the extractive matter which the open mashing involves if the percentage of the exhausted grains is unknown.

M. J. S.

**Rapid Technical Analysis of Pale and Dark Peats.** By HUGO BORNTÄGER (*Zeit. anal. Chem.*, 1901, 40, 639—641).—Nitrogen, moisture, and woody fibre are the only substances estimated. Moisture is estimated by drying at 110°; air-dried peat contains about 20 per cent. Pale coloured peat (5 kilograms) is heated with water (2 kilos.) at 5 atmospheres pressure for 5 hours in a digester (*Dampf-Druckfilter*); the insoluble fibres are pressed with a screw-press, dried at 110°, and weighed. The evaporated extract yields about 22

per cent. of a saccharin substance, which can be used as a feeding stuff for cattle (compare D.R.-P. 122193).

Dark peat, from which sugar is not obtainable, is similarly digested with addition of 800 grams of potash. The fibre is weighed as before, and the difference is regarded as humic acid; the proportion varies from 25 to 60 per cent. The humic acid is a valuable disinfectant; it is also the constituent on which the calorific value of a peat chiefly depends.

M. J. S.

**The Red Solution of Gold as a Reagent for Colloids.** By RICHARD ZSIGMONDY (*Zeit. anal. Chem.*, 1901, 40, 697—719).—The red solutions of metallic gold, obtained by reducing auric chloride by formaldehyde in presence of a weak alkali (Abstr., 1898, ii, 522), which the author regards as colloidal solutions (Abstr., 1900, ii, 397), become blue when mixed with sodium chloride (also other salts, acids, and alkalis), in consequence of an agglomeration of the particles of gold. This change of colour is prevented by the presence of a sufficient quantity of certain other colloids, and a classification of colloid substances can be made according to the amount required to prevent the change of colour, since the differences amongst them have a very extensive range. The author suggests the establishment of a "gold number," as a characteristic of each class of colloids, the process of estimation being as follows.

*Preparation of the Reagent.*—120 c.c. of water (twice distilled through a silver condenser) are boiled up in a Jena glass beaker; 2.5 c.c. of a 0.6 per cent. solution of chloroauric acid, ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ), and 3—3.5 c.c. of 0.18*N* potassium carbonate, and then, slowly, 3—5 c.c. of a solution of commercial formalin (0.3 c.c. in 100 c.c. of water) are added. The red colour is developed in a few seconds. Turbid or purplish solutions are only fit for qualitative testing.

*Mode of Testing.*—The solution of the colloid (not more than 2 c.c.) is mixed with 10 c.c. of the gold solution and then 1 c.c. of a 10 per cent. solution of sodium chloride is added. The change of colour, if any, occurs immediately, and fresh experiments with different amounts of the colloid solution are made until the quantity is ascertained, which is just insufficient to prevent the change of colour. The results are expressed in milligrams of the colloid employed.

In the first or most active class, substances are placed which have a gold number of 0.005—0.1, such as gelatin. The second class contains substances of which 0.1—10 mg. are required, such as gum arabic, egg-albumin, tragacanth, and Iceland moss. Substances are placed in the third class, when 10—500 mg. are necessary, dextrin and potato starch, for instance. The fourth class contains such substances as colloidal silicic acid, which, in any quantity, will not prevent the change of colour.

Solutions should be examined when freshly prepared; all colloidal solutions seem to diminish in activity with age, although at very different speeds. Various applications of the new method are suggested.

M. J. S.

## General and Physical Chemistry.

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**Use of Helium in Spectroscopy.** By ARMIN TSCHERMAK (*Pflüger's Archiv*, 1901, **88**, 95—97).—The author recommends the bright lines produced by the incandescent helium spectrum in a Plücker tube containing aluminium electrodes as one of the most convenient methods for wave-length determinations. The following lines are visible and most are well developed: 707, 688, 587·6, 502, 495, 470, 446. The same apparatus is also recommended as a source of light in determination of refractive indices, &c. J. J. S.

**Banded Flame Spectra of Metals.** By WALTER NOEL HARTLEY and HUGH RAMAGE (*Sci. Trans. Roy. Dublin Soc.*, 1901, [ii], **7**, 339—352).—A continuation of previous work (*Phil. Trans.*, 1894, **185**, A, 161—212). Metals of very different characters belonging to different groups in the periodic system yield banded spectra or spectra showing both bands and distinct lines. Examples are magnesium, zinc, and cadmium; copper, silver, and gold; aluminium, indium, and thallium; palladium and iridium; bismuth, tin, and lead. Banded spectra are given by metals which are combustible with large development of heat forming slightly volatile oxides, by metals yielding easily volatile oxides, and by metals that do not form oxides at the temperature of the flame. Certain groups of elements (copper, silver, and gold; aluminium and indium; beryllium and lanthanum) give banded spectra which are degraded towards the less refrangible rays; in other spectra (magnesium, zinc, cadmium), the bands are degraded on the other side. The flame spectra of palladium and iridium show many lines, independent of the fine lines making up the bands: this feature is probably connected with the difficulty of volatilising these metals in the oxy-hydrogen flame. Elements belonging to the same group in the periodic system exhibit similarly constituted banded spectra; hence similarly constituted molecules of the elements have similar modes of vibration, whether at the lower temperature of the flame or at the higher temperature of the arc. J. C. P.

**Spectra of the Rare Earths.** By ABRAHAM LANGLET (*Bihang K. Svenska Vet.-Akad. Handl.*, 1901, **26**, ii, No 2, 1—16).—From a number of observations on the spectra of solutions of praseodymium salts, the author draws the following conclusions. For concentrated aqueous solutions of praseodymium salts, Bunsen's law concerning the relation between the intensity of the absorption bands and the optical concentration does not hold good. In concentrated solutions, the absorption in the yellow is both relatively and absolutely weaker than with dilute solutions, whilst the absence of maxima makes the bands more indistinct. The same action is observed with many ammonium and lanthanum-ammonium salts, whilst lanthanum salts show a similar but slighter action. The presence of a large quantity of

nitric acid weakens all the absorption bands with the possible exception of the last band in the blue; here also the absorption in the yellow is affected to the greatest extent. Solutions of praseodymium carbonate and tartrate in alkalis yield perfectly identical spectra, which, however, differ considerably from those of salt solutions of the same concentration. Benzene solutions of organic praseodymium compounds give varying spectra, which also differ widely from those of the neutral salts.

T. H. P.

**Ultra-violet Absorption Spectra.** By G. PAUL DROSSBACH (*Ber.*, 1902, 35, 91—93).—The author, in determining how far certain substances (mostly in 10 per cent. solution) absorb the ultra-violet rays, finds a marked absorption in the case of some salts of heavy metals, nitrates, and organic substances with high molecular weight. Hydrochloric acid, sulphuric acid, potassium chloride, chlorate and sulphate, sodium and calcium chlorides, aluminium and manganese sulphates, are found to be colourless, that is, light up to  $230\mu$  passes through these as easily as through water. In the following cases, where absorption takes place, the number gives the length of the shortest wave which can pass through: nitric acid, 340; oxalic acid, 294; potassium carbonate, 244; potassium oxalate, 294; potassium nitrate, 340; ammonia, 272; barium chloride, 236; barium nitrate, 340; aluminium nitrate, 340; zinc chloride, 290; ferrous sulphate, 394; ferric chloride, 400; nickel chloride, 400; lead acetate, 294; chromium chloride, 390; uranium chloride, 400; manganese nitrate, 340; copper sulphate, 296. It is to be noted that the salts of colourless metals give the spectra of the corresponding acids; thus the limit for all such nitrates is 340.

J. C. P.

**Radioactive Substances.** By P. CURIE and SŁODOWSKA CURIE (*Compt. rend.*, 1902, 134, 85—87).—The various observations hitherto made show that in the case of uranium, thorium, radium, and probably actinium, the radioactivity is always the same when the radioactive substance is brought into the same chemical and physical state, and it does not vary with the time. If, by any particular treatment, the substance loses some of its activity, it subsequently regains it in course of time. Polonium behaves differently from other radioactive substances. The absence of any evidence that the intensity of the radioactivity diminishes with time, or that the substances undergo any loss of weight, indicates that the energy of the radiation may either be derived from heat radiations in some manner contrary to Carnot's principle, or from some other source, possibly radiations not hitherto recognised by any other means.

C. H. B.

**Existence of Rays which undergo Reflection in the Radiations emitted by a Mixture of Chlorides of Radium and of Barium.** By THOMAS TOMMASINA (*Compt. rend.*, 1901, 133, 1299—1301).—The author shows that some of the radiations can be reflected by a parabolic mirror of silvered copper, the reflection being evidenced by increase in the rate of discharge of an electroscope.

L. M. J.

**Law of Transparency of Matter for X-Rays.** By L. BENOIST (*J. Physique*, 1901, 10, 653—668).—As a measure of the transparency, the author has determined for a large number of compounds and elements what he terms the equivalent of transparency, which is the mass in decigrams of a prism having a base of 1 sq. cm. which, when traversed along its axis by the X-rays, produces the same absorption as a prism of paraffin 75 mm. in height. It is found that the specific opacity of a substance is independent of its physical state, this being verified for bromine, ethyl bromide, methyl iodide, and other compounds; it is, further, independent of temperature, and holds for the crystalline and amorphous states. The opacity is further independent of the atomic or molecular grouping, being, hence, equal for isomerides, polymerides, or various allotropic forms. It is independent of combination of the atoms, being a *purely additive quantity*, so that the opacity of a compound may be readily calculated. Thus, if  $M$  is the total mass of a compound or mixture and  $E$  its equivalent of transparency, and  $m_1 m_2 \dots e_1 e_2 \dots$  are the similar constants for the components, then  $\frac{M}{E} = \frac{m_1}{e_1} + \frac{m_2}{e_2} \dots$  and various illustrative examples are given, thus quartz, calculated from the values of silicon and oxygen, should have the equivalent 24; that found was 24.1. The opacity increases with the atomic weight, and a curve constructed with the equivalents of transparency as ordinates against atomic weight as abscissæ is perfectly continuous, being of form approximating to a hyperbola. It is evident, hence, that the equivalent might be of use in determining an atomic weight, and it is shown, for example, that the atomic weight of indium must be very nearly equal to those of silver and cadmium. The transparency varies with the nature of the rays, but it is remarkable that this variation is very slight for silver and elements the atomic weights of which lie near its value. The author suggests also that this purely additive quantity might be of use in certain cases of quantitative analysis.

L. M. J.

**Behaviour of Aldehydes and Ketones towards Tesla-rays.** By HUGO KAUFFMANN (*Ber.*, 1902, 35, 473—483).—Aldehydes and ketones alone amongst aliphatic compounds resemble certain aromatic compounds in emitting blue light when exposed to Tesla-rays. The carbonyl group is responsible for this effect, which is very marked in the case of formaldehyde as well as in the ketones where the carbonyl is linked to two carbon atoms, but no such effect is produced by the carbonyl group in acids, esters, anhydrides, or amides. The effect also disappears in the case of aldehydes and ketones as soon as the carbonyl group is displaced, as in acetoxime and the acetals.

The intensity of the radiation is diminished by increasing the number of carbon atoms in the molecule, by the entrance of a carboxy-group, and in a still more marked degree by the introduction of a phenyl group. Diacetyl and acetonylacetone are luminescent, showing that amongst aliphatic compounds, colour and luminescence can occur together, but acetylacetone shows no luminescence, possibly by reason of its conversion into an enolic modification. Saturated ring-ketones are luminescent, but not those which contain double linkings.



Like the benzene nucleus, it is probable that the carbonyl group can exist in an active or in an inactive condition, and that this determines the presence or absence of luminescence; chemical activity and luminescence would then be parallel phenomena. T. M. L.

**Importance of Electrical Methods and Theories in Chemistry.** By WALTHER NEERNST (*Zeit. Elektrochem.*, 1901, 7, 1004—1006).—After passing in review the well-known theories of electrochemistry, the author points out that they all lead to the view that electricity consists of positive and negative electrons, which may combine (1) with matter to form compounds (the ions) which differ widely from the original matter, or (2) with each other to form a neutral electron molecule. This leads to the following theory of chemical combination; all elements and radicles possess affinity for positive or negative electrons, with which they unite to form the ions; they also possess non-polar attraction for each other, to which the formation of compounds of the metals, of hydrogen molecules, of iodine chloride, for example, is due. When a positive element combines with a negative one, however, an electron molecule is added, and this separates into its positive and negative electrons when the molecule is ionised. Such compounds differ much more from their constituents than those which contain no electron molecule. For example, the compounds of metals are metallic, those of non-metals retain the characters of non-metals, whilst a compound of a metal and a non-metal is a substance belonging to a new class altogether. It is possible that elements exist which combine with the positive electrons, without the negative electrons being simultaneously taken up by another substance; in this case, the negative electrons might be set free and appear as the Becquerel rays. T. E.

**Electrode Potentials.** By FRITZ HABER (*Zeit. Elektrochem.*, 1901, 7, 1043—1053).—The potentials of metallic or non-metallic electrodes are usually expressed in a uniform way, but this is not the case with the so-called oxidation and reduction electrodes. By means of the following formula, the derivation of which is given, all electrode potentials ( $E$ ) may be expressed in a uniform manner:

$$E = \frac{RT}{\nu F} \left[ \log K - \log \frac{[A']^{m'} [B']^{n'} \dots}{[A]^m [B]^n \dots} \right],$$

where  $\nu$  electrons,  $F$ , are taken up in the conversion of  $m'$ ,  $n'$  ... molecules of the substances  $A'$ ,  $B'$  ... in the concentrations  $[A']$ ,  $[B']$ , &c., into  $m$ ,  $n$ , &c., molecules of the substances  $A$ ,  $B$ , &c. This applies to an oxidation; for a reduction, the sign is changed throughout the equation, the sign of  $E$  applying always to the solution.  $K$  is the equilibrium constant of the reaction occurring at the electrode. When all the concentrations of the gaseous and dissolved substances are unity, the second logarithm disappears and  $E = RT/\nu F \log K = ep_T$ , where  $ep_T$  is what Wilsmore (*Abstr.*, 1901, ii, 2 and 142) has called the electrolytic potential at temperature  $T$ . This may be referred to the hydrogen electrode, or to the absolute value of the calomel electrode. The detailed application of the equation to the more important cases which have been investigated, which is made in the original, does not admit of brief abstraction. T. E.

**Electromotive Force of Metals in Cyanide Solutions.** By S. B. CHRISTY (*Chem. Centr.*, 1901, ii, 1326; from *Elektrochem. Zeit.*, 1901, 8, 181—186).—The electromotive force of a cyanide solution against copper decreases with decrease of concentration. For potassium cyanide against copper, the values are +0.9 volt for *N* solutions and -0.3 volt for *N*/1,000,000 solutions; for zinc, the values similarly decrease from +1 volt to -0.6 volt; for gold from 0.4 volt to -0.622 volt. With the latter metal in *N* potassium chloride and *N* potassium hydroxide solutions the values are respectively -0.487 and -0.381.

L. M. J.

**Electrolysis of Alkali Chlorides with Carbon Anodes.** By L. SPROESSER (*Zeit. Elektrochem.*, 1901, 7, 971—976, 987—994, 1012—1017, 1027—1035, 1071—1076, and 1083—1093).—The nature, extent, and causes of the deterioration of carbon anodes of different kinds when used in the electrolysis of solutions of alkali chlorides are investigated very fully. Cells with and without diaphragms were used, and the solution always contained more or less chlorate and hypochlorite.

The attack of the carbon is mainly due to oxidation, chlorination occurs sometimes with carbons containing volatile matter, but it is in general of very little importance. The principal oxidation product is carbon dioxide; considerable disintegration of the carbon always occurs, the loss due to which may exceed that due to the chemical action. The difference between the results of experiments with and without diaphragms is one of degree, the concentration of the hypochlorite and the oxidation being smaller in the former case.

In sulphuric acid (about 20 per cent.  $\text{H}_2\text{SO}_4$ ), more than 90 per cent. of the oxygen separated at the anode is used in oxidation of the carbon, about half of it yielding carbon dioxide, and the remainder, probably colloidal, humus-like substances which colour the acid brown (the same products are formed with the other electrolytes although in different proportions). The mechanical disintegration of the carbon is very marked. With a 16 per cent. solution of sodium hydroxide, both oxidation and disintegration are less than with sulphuric acid, and different specimens of carbon behave differently, which was not the case with the acid. There is no direct relation between the behaviour of carbon in the different solutions. Rise of temperature always accelerates the destruction of the carbon.

The author explains the characteristic behaviour of the carbon anodes by their porous nature. When a solution of an alkali chloride is electrolysed, the Cl ions within the pores of the carbon are soon discharged, and since they cannot be rapidly replaced by diffusion, a point is soon reached at which OH ions are discharged. This only occurs within the pores, because the circulation of the electrolyte at the surface of the anode keeps up a sufficient supply of Cl ions there. The carbon is therefore oxidised mainly within the pores, which explains the disintegration observed. The disintegration is not due to the escape of gas, because a carbon cathode does not disintegrate. In similar circumstances, much more oxygen is evolved from a carbon anode than from one of platinum, a fact readily explained by the

author's hypothesis. This is strikingly exemplified by a series of experiments with hydrochloric acid in which the quantity of oxygen evolved increases with the porosity of the carbon anode used. That the concentration of hypochlorite attainable at a carbon anode is much smaller than at one of platinum is also in agreement with the theory, because for each OH ion discharged a H ion must remain in solution. This is equivalent to the formation of a molecule of hydrogen chloride, which decomposes an equivalent quantity of hypochlorite. A carbon anode undergoes great disintegration in sulphuric acid of moderate concentration, but is very little disintegrated in concentrated acid; since the discharge of  $\text{SO}_4$  ions within the pores of the carbon increases the strength of the acid contained in them, it will be a better or worse conductor than the main body of the acid according as this is weaker or stronger than the acid of maximum conductivity. The pores will therefore be more exposed to attack in weak acid and less exposed in strong acid.

The formation of hydrogen chloride at carbon anodes may be explained by the reaction  $2\text{HOCl} + \text{C} = 2\text{HCl} + \text{CO}_2$ . The author shows that this change really occurs with considerable velocity, but inclines to the view that his own hypothesis is preferable as being more generally applicable.

Generally speaking, the less porous a carbon the more suitable it is for use in the electrolysis of solutions of alkali chlorides, but the only satisfactory test of the suitability of a carbon is a prolonged experiment with it under working conditions.

T. E.

**Electrocapillary Maxima of some Organic Compounds.** By A. GOUY (*Compt. rend.*, 1901, 133, 1301—1303).—The depression of the electrocapillary maximum by the dissolution of various organic compounds was studied, and it was found that the depression increases less rapidly than the concentration. The maxima with liquids almost anhydrous and only containing sufficient water to render them conductive were also found. Fifty liquids were examined and it was observed that in general the depression is greatest for "active" compounds. With these also, the depression is only double or treble what is obtained in solutions of about 1 per cent., a fact which further supports the supposition of the accumulation of the active ions at the mercurial surface (*Abstr.*, 1901, ii, 83).

L. M. J.

**Apparatus for the Demonstration and Determination of Ionic Mobilities.** By RICHARD ABEGG (*Zeit. Elektrochem.*, 1901, 7, 1011—1012).—A somewhat simplified form of the apparatus used by Steele (*Trans.*, 1901, 79, 414) is described. The tubes are enclosed in a vessel, with plate glass sides, containing water, so that the movement of the boundary surfaces of the solutions can be shown to an audience by means of the lantern.

T. E.

**Thermometer of Light Petroleum.** By L. BAUDIN (*Compt. rend.*, 1901, 133, 1207).—The author has successfully employed a thermometer in which the liquid is light petroleum, of sp. gr. 0.647 at  $15^\circ$ , to record temperatures as low as that of liquid air, in which

it remains unfrozen. The graduation was obtained by the use of melting ice, and boiling methyl chloride, nitrous oxide, and oxygen.

L. M. J.

**Method of determining Latent Heat of Evaporation.** Latent Heat of Evaporation of Pyridine, Acetonitrile, and Benzonitrile. By LOUIS KAHLBERG (*J. Physical Chem.*, 1901, 5, 215—232).—The method is practically identical with that employed by Berthelot (*Abstr.*, 1878, 106), the only essential difference being the use of an electric current for heating the liquid. The values obtained for the specific heat and latent heat of evaporation of the carefully purified compounds are as follows: Pyridine, specific heat, 0·4313; latent heat, 104·0; acetonitrile, specific heat, 0·5333; latent heat, 173·6; benzonitrile, specific heat, 0·4369; latent heat, 87·7. The values obtained for the boiling point constants by use of these numbers are respectively 28·8, 48·67, and 14·39, agreeing fairly with those calculated by Trouton's rule, namely, 29·5, 45·7, and 13·9. L. M. J.

**Critical Constants and Molecular Complexity of Hydrocarbons.** By PHILIPPE A. GUYE and ED. MALLET (*Compt. rend.*, 1901, 133, 1287—1290).—The following values have been obtained by the authors:

	$T_c$ .	$p_c$ .	$K_c$ .	$a \times 10^{-6}$ .	$b$ .
Durene .....	675·5	28·6	23·62	45·36	242·4
Diphenylmethane .....	770·0	28·2	27·30	38·25	224·1
Diphenyl.....	768·6	31·8	24·17	52·81	248·0
Naphthalene .....	741·2	39·2	18·89	39·79	193·8

$T_c$  is the absolute critical temperature,  $p_c$  the critical pressure in atmospheres,  $K_c$  the critical coefficient =  $T_c/p_c$ ;  $a$  and  $b$  are the values of these constants in Van der Waals' equations calculated for the molecular weight in grams, volumes being expressed in cubic centimetres. To determine molecular complexity in liquid and vapour phases, the following quantities are examined: (1) Ratio of molecular refraction  $(n^2 - 1)M/(n^2 + 2)D$  to the critical coefficient  $K_c$ . (2) Ratio of the real to the theoretical critical density. (3) The value of the constant  $(\log p_c - \log p)T/(T_c - T)$ , where  $T$  is the boiling point at pressure  $p$ . The values of these three quantities are respectively, durene, 1·86, 4·09, 3·17; diphenylmethane, 1·96, 4·08, 3·29; diphenyl, 2·05, 4·26, 3·27; naphthalene, 2·22, 3·88, 3·13.

Polymerisation may be established by the following. The liquid is polymerised at the critical point if the ratio (1) is distinctly below 1·8 and (2) greater than 4·0. The complexity is normal between boiling point and critical point if (1) = about 1·8, (2) = about 3·9 or 4, and (3) = about 3·1. If, however, (3) is greater than 3·1, it indicates polymerisation of the liquid phase at low temperatures with depolymerisation in the vapour phase at the critical temperature. The hydrocarbons examined hence appear normal from ordinary conditions to the critical conditions.

L. M. J.

**Criticisms on Melting Point Determinations.** By M. C. SCHUYTEN (*Chem. Centr.*, 1901, ii, 1326; from *Hand. vijfde Vlaamsch*

*Natur-Genesskund. Congres.*, 1901).—Values given by different observers for the melting point of a compound frequently differ greatly and the observed melting point is influenced considerably by conditions of the experiment, such as size of flame, rapidity of heating, nature of the thermometer glass, &c. With stearin, the author obtained results varying from  $27^{\circ}$  to  $57.5^{\circ}$ , and he considers that most of the melting point data are not absolutely trustworthy.

L. M. J.

**Determination of the Solidifying Point of Fats.** By AL. A. SHUKOFF (*Chem. Zeit.*, 1901, 25, 1111—1112. Compare Abstr., 1899, ii, 588).—The author now recommends a modification of the apparatus previously used (*loc. cit.*) for the determination of the solidifying point of fats and oils. For substances which solidify below the ordinary temperature, an apparatus closely resembling Beckmann's apparatus for cryoscopic measurements is used. The temperature of the cooling liquid in the outermost vessel must only be  $2^{\circ}$  or  $3^{\circ}$  below the solidifying point of the substance under investigation.

K. J. P. O.

**Minimum Boiling Points and Vapour Composition. II.** By MORRIS R. EBERSOLE (*J. Physical Chem.*, 1901, 5, 239—255).—A continuation of a previous paper by Pettit (Abstr., 1899, ii, 632). Ryland's observation (Abstr., 1900, ii, 64) that acetone and benzene in the ratio 5 to 1 tended "to gather" at the boiling point  $57$ — $58^{\circ}$ , led to the investigation of the boiling point curve and of the composition of the vapour phase. The boiling point curve is normal, and at no point is the composition of the vapour identical with that of the liquid, although at the lower part of the curve the composition of the vapour approaches closely to that of the liquid; this explains "the tendency to gather at  $57$ — $58^{\circ}$ ." The known data regarding vapour pressure curves and boiling point curves of mixtures are collected and classified in order to see how far Bancroft's rule is valid. Five mixtures form exceptions to the rule as they have intersecting vapour pressure curves, but normal boiling point curves without maximum or minimum. These are acetone and ethyl alcohol, propyl alcohol and ethyl acetate, benzene and carbon tetrachloride, benzene and ethyl acetate, benzene and isobutyl alcohol. Repetition of observations seems here desirable. Four cases occur in which a minimum boiling point is obtained with non-intersecting vapour pressure curves.

L. M. J.

**Molecular Weights of certain Salts in Acetone.** By HARRY C. JONES (*Amer. Chem. J.*, 1902, 27, 16—22).—The rise in the boiling point of acetone when varying quantities of cadmium iodide, ammonium thiocyanate, mercuric chloride, or sodium iodide are dissolved in it has been determined. The molecular weights found for cadmium iodide (366) vary from 448 to 510, and of ammonium thiocyanate (76.2) from 88 to 102, showing that in these cases the molecules are associated. As the solutions possess an appreciable conductivity (Dutoit and Aston, Laszczynski), there must be at the same time a certain amount of dissociation. The molecular weight found for mercuric chloride is almost exactly normal, and the

solution has practically no conductivity (Laszczynski). For sodium iodide (149.9) the molecular weights vary from 133 to 143. The conductivity has not been determined at the dilutions at which the boiling point experiments were carried out.

The author's results are not in agreement with those of Dutoit and Friderich (Abstr., 1899, ii, 350). J. McC.

**Application of Optical Observations to the Study of Diffusion.** By J. THOVERT (*Compt. rend.*, 1901, 133, 1197—1199).—If a horizontal beam of light penetrates into a parallelepiped containing two superposed solutions of the same salt at different concentrations, it is deviated, and from the observation of this deviation at various time intervals the diffusion may be deduced. The results of experiments based on such observations are, however, postponed.

L. M. J.

**Rate of Hydration of Metaphosphoric Acid.** By J. C. BLAKE and F. C. BLAKE (*Amer. Chem. J.*, 1902, 27, 68—74).—The velocity of hydration of metaphosphoric acid was measured by the method described by Duane (Abstr., 1901, ii, 440), which is based on the change of refractive power of the medium in which the reaction takes place. The hydration in a solution containing 4 grams of metaphosphoric acid and 5 c.c. of water is complete in about 4 days at 18.5°. J. McC.

**Conditions of Equilibrium of Deliquescent and Hygroscopic Salts of Copper, Cobalt, and Nickel, with respect to Atmospheric Moisture.** By W. NOEL HARTLEY (*Sci. Trans. Roy. Dublin Soc.*, 1901, [ii], 7, 313—320. Compare Hartley, Abstr., 1901, ii, 53).—The quantity of water attracted by cupric chloride and bromide, cobalt chloride and bromide, nickel bromide and iodide, under varying conditions of temperature and aqueous vapour pressure, was determined at intervals of a few days over a period of six months. The bromides were found to be more deliquescent than the chlorides, and the iodides than the bromides. The most stable liquid hydrates are those of nickel iodide with 23 and 21 mols. of water; then cobalt bromide and nickel bromide with 18 mols., cobalt chloride with 11 mols., cupric bromide with 4 mols., and cupric chloride with 3 mols. The attraction of the salt for water is independent of the molecular mass of the salt; thus cobalt chloride absorbs more water than cupric chloride; cobalt and nickel bromides absorb more water than cupric bromide.

Cobalt iodide was also investigated, but no figures are given because the salt is decomposed by light. It is so deliquescent that in a moist atmosphere it increases in weight more rapidly than sulphuric acid.

J. C. P.

**Catalysis.** By WILHELM OSTWALD (*Zeit. Elektrochem.*, 1901, 7, 995—1004).—Four classes of catalytic actions are distinguished, namely, those in (1) supersaturated systems, (2) homogeneous systems, (3) heterogeneous systems, (4) actions of enzymes. In the first class, a more stable system exists, which differs from the unstable super-

saturated system by containing a new phase. In general, the new phase cannot be formed spontaneously, but the addition of a very minute quantity of it suffices to initiate the change. The substance of which the new phase consists is not necessarily present in the system; dilute solutions of lead salts and thiosulphates, for example, behave as though they were supersaturated with lead sulphide. Owing to the small amount of the catalytic agent required, it can add no energy to the system; the change must therefore be accompanied by a diminution of free energy (not necessarily by a development of heat). This applies equally to all changes taking place under the influence of a catalytic agent, and such changes can only occur in unstable systems. An unstable homogeneous system can only exist in a condition of change, which change may, however, be so slow as to escape recognition. A catalytic agent accelerates or retards the change, without itself forming a constituent of the initial or final products. Apparently all kinds of substances may act as catalysers, and all kinds of reactions may be influenced by them. Liebig's view that catalysis is due to molecular vibrations communicated to the reacting substances by the catalyser, is rejected as being incapable of proof or disproof. The theory of intermediate products is not contradicted by the laws of chemical kinetics, although it has never been proved that the velocities of the partial reactions were greater than that of the direct reaction, and until this is done the theory can only be regarded as a possible explanation. In any case, it cannot explain all catalyses, especially those in which a reaction is retarded. Heterogeneous catalyses, those in presence of platinum, for example, are also probably accelerations of slow reactions, possibly due to condensation of gaseous substances. The action of enzymes is entirely analogous to the action of the simpler catalytic agents. In the animal body, where the temperature is practically constant, and the concentrations of the reacting substances can vary within comparatively narrow limits, the velocities of the different reactions, on the exact balance of which the maintenance of life depends, are regulated by means of enzymes. The study of catalysis from this point of view is of the utmost interest. T. E.

**Dilution Constant of Saline Solutions.** By ALBERT COLSON (*Compt. rend.*, 1901, 133, 1207—1209).—At certain temperatures, dilution of a solution produces no thermal change, and this temperature had been previously found for dilute solutions (25 grams per litre) of sodium chloride. The researches have been extended to saturated solutions about 10 times as concentrated, but the value for the inversion point is the same as that previously found, namely, 52°. For strong solutions of potassium chloride, the value obtained was 64.5°; for sodium nitrate 116° (by extrapolation), and potassium nitrate about 122° (by extrapolation) (compare this vol., ii, 4). L. M. J.

**Saturated Solutions of Salts of Analogous Series.** By CARLO ROSSI (*Gazzetta*, 1901, 31, ii, 502—510).—A comparison of the solubility coefficients of analogous salts shows that the ratio of the molecular weights of two salts is an integral multiple of the ratio between the corresponding solubility coefficients at a certain temperature, the

solubility coefficient being the number of grams of a compound dissolved by 100 grams of water and analogous salts being such as have one ion common whilst the other ions are analogous in the sense of the periodic law. This is shown by the numbers in the following table :

Pairs of salts.	Molecular weights.	Solubility co-efficients.	Ratio between the		Ratio of A to B.	Difference.
			Molecular weights (A).	Solubility co-efficients (B).		
{ BaCl <sub>2</sub> .....	208	35·7	1·318	0·66	2	0·01
{ SrCl <sub>2</sub> .....	158	53·9				
{ BaCl <sub>2</sub> .....	208	35·7				
{ CaCl <sub>2</sub> .....	111	74·01	1·87	0·482	4	0·048
{ SrCl <sub>2</sub> .....	158	53·9	1·42	0·72	2	0·02
{ CaCl <sub>2</sub> .....	111	74·01				
{ BaBr <sub>2</sub> .....	297·32	98·03				
{ SrBr <sub>2</sub> .....	247·52	87·71	1·201	1·117	1	0·034
{ BaBr <sub>2</sub> .....	297·32	98·03	1·417	0·784	2	0·081
{ CaBr <sub>2</sub> .....	199·92	125				
{ SrBr <sub>2</sub> .....	247·52	87·71				
{ CaBr <sub>2</sub> .....	199·92	125	1·238	0·701	2	0·168
{ Ba(NO <sub>3</sub> ) <sub>2</sub> ..	261·4	9·2	1·235	0·1256	10	0·021
{ Sr(NO <sub>3</sub> ) <sub>2</sub> ..	211·6	70·8				
{ KCl .....	74·5	29·2				
{ LiCl .....	42·47	63·6	1·75	0·45	4	0·05
{ KBr .....	119	53·48	1·368	0·373	4	0·124
{ LiBr .....	87	143				
{ KI .....	166	209				
{ LiI .....	134	47·6	1·23	0·43	3	0·06
{ CoSO <sub>4</sub> ...	155·06	60·4	1·001	1·055	1	0·054
{ NiSO <sub>4</sub> ...	154·76	57·2				

Hence the saturated solutions of analogous salts at one and the same temperature are equal molecular solutions or else there is a simple relation between the numbers of molecules of the different salts dissolved by the same number of water molecules. From the numbers in the above table, it can be calculated that the number of molecules of water required to dissolve 1 mol. of salt are, for barium, strontium, and calcium chloride, 32, 16, and 8 respectively, so that the numbers of molecules of the salts which saturate the same quantity of water stand in the relation of 1 : 2 : 4. Similar relations are exhibited by the other sets of analogous salts given in the table. Further, the ratio between the molecular volumes of a pair of analogous salts is a simple multiple of the ratio between the volumes of the solubility coefficients ; for the alkaline earth chlorides, these relations are shown in the table on p. 200 :

It is readily shown, further, that the molecular volumes of saturated solutions of salts of analogous series have the same values at a definite temperature. Such saturated solutions are regarded by the author as representing, at any definite temperature, true chemical compounds,



	Molecular volumes.	Volume of solubility coefficients.	Ratio of molecular volumes.	Ratio of solubility coefficient volumes.
{ BaCl <sub>2</sub> .....	54·2	9·27	1·04	0·52
{ SrCl <sub>2</sub> .....	51·7	17·61		
{ BaCl <sub>2</sub> .....	54·2	9·27	1·08	0·27
{ CaCl <sub>2</sub> .....	50·09	33·39		
{ SrCl <sub>2</sub> .....	51·7	17·61	1·03	0·52
{ CaCl <sub>2</sub> .....	50·09	33·39		

which are liquid and readily dissociated, being destroyed by the very slightest change in temperature.

T. H. P.

**Theory of the Molecular Constitution of Supersaturated Solutions.** By W. NOEL HARTLEY (*Sci. Proc. Roy. Dublin Soc.*, 1901, 9, 529—542).—In the author's opinion, the hydrate existing in a so-called supersaturated solution is not the same as the hydrate which crystallises out; the phenomenon of supersaturation is a manifestation of a difference in the solubilities of two distinct hydrates at a given temperature. From a study of copper sulphate, cobalt iodide, and cupric bromide, it appears that an anhydrous salt must become hydrated before it can pass into solution. The author finds confirmation of his views in the behaviour of coloured salt solutions, particularly cupric bromide and cobalt chloride. Nicol's work and views (*Abstr.*, 1898, ii, 369) are discussed, and compared with the author's (see also Hartley, *Abstr.*, 1901, ii, 53; Wyruboff, *ibid.*, 149).

J. C. P.

**Clearing of Turbid Solutions.** By GEORG QUINCKE (*Ann. Phys.*, 1902, [iv], 7, 57—96).—The author's results are summarised as follows. Water, containing in suspension gum mastic, gamboge, shellac, oleic acid, and similar substances, is cleared by the addition of very small quantities of an acid or a salt solution. In the process, the particles unite to form flocks, and settle at the bottom or on the sides of the containing vessel. The flocks consist of drops and bubbles of the substance in the liquid or solid state, and usually enclose more or less air. The formation of flocks and the final clearing of the solution are due to a periodic distribution of small quantities of the clarifying liquid on the surface of the suspended particles; this produces eddies in the surrounding fluid and drives the particles against each other and against the walls of the containing vessel. Both electrolytes and non-electrolytes may act as clarifying agents. The relative velocities of clarification induced by different agents alter with the quantity and nature of the suspended substance. The flocks covered with a layer of clarifying liquid must be nearly isoelectric with the surrounding fluid, and therefore cannot be electrically displaced (compare Hardy, *Proc. Roy. Soc.*, 1900, 66, 111). The flocks may be deposited on either the light or the dark side of a vessel, according to the distribution of the clarifying liquid. The silverising of glass by chemical methods is a particular case of the clarification of a turbid solution.

J. C. P.

**Periodic Classification of the Elements.** By HEINRICH BILTZ (*Ber.*, 1902, 35, 562—568).—To simplify the classification, the author suggests inserting a group of elements in place of a single element, for example, Mn, Fe, Co, Ni, in place of manganese. The groups thus made are  $\Sigma\text{Ce} = \text{La, Ce, Pr, Nd}$ ;  $\Sigma\text{Fe} = \text{MnFe, Co, Ni}$ ;  $\Sigma\text{Pd} = \text{Ru, Rh, Pd}$ ;  $\Sigma\text{Pt} = \text{Os, Ir, Pt}$ . The new atmospheric elements are placed in group 1;  $\Sigma\text{Ce}$  occupies the 7th place in group 4;  $\Sigma\text{Fe}$ ,  $\Sigma\text{Pd}$ , and  $\Sigma\text{Pt}$  positions 3, 5, and 8 in group 8.

He	Li	Be	B	C	N	O	F
Ne	Na	Mg	Al	Si	P	S	Cl
Ar	K	Ca	Sc	Ti	V	Cr	$\Sigma\text{Fe}$
	Kr	Cu	Zn	Ga	Ge	As	Se
X	Rb	Sr	Y	Zr	Nb	Mo	$\Sigma\text{Pd}$
		Ag	Cd		Sn	Sb	Te
	Cs	Ba	$\Sigma\text{Ce}$ Yb		Ex Ta	W	$\Sigma\text{Pt}$
		Hg	Tl	Pb Th	Bi U		

J. J. S.

**Prout's Hypothesis and the Tendency of Atomic Weights to approach Whole Numbers.** By MAX RUDOLPHI (*Chem. Zeit.*, 1901, 25, 1133—1134).—The deviation of atomic weights from whole numbers is attributed to the presence of small quantities of unknown elements, the properties of which are closely allied to those of the element with which they are respectively mixed (compare Booth, *Chem. News.*, 1901, 83, 262).

K. J. P. O.

**New Construction of Laboratory Hood.** By JOSEF HABERMANN and A. OESTERREICHER (*Zeit. anal. Chem.*, 1901, 40, 767—768).—Instead of the single, comparatively small, circular or square opening by which, in most laboratories, the hood communicates with a chimney, this hood has a number of vertical slits at the back, communicating with a common flue. The consequence is that all parts of the hood are equally ventilated, which is not the case with the usual construction.

M. J. S.

**Simple Condenser.** By JOSEF HABERMANN and A. OESTERREICHER (*Zeit. anal. Chem.*, 1901, 40, 769—770).—The tube in which condensation is to take place has a vertical position. Round it is wrapped a layer of stout, porous paper, which at the upper end is thickened until it fits the neck of a water reservoir made by cutting off the bottom of a bottle. Sufficient water percolates through this plug to keep the paper jacket wet, and the evaporation of the water from the paper is the principal factor in the cooling process. Any excess of water is caught by a funnel near the bottom of the tube and may be returned to the reservoir even if it is warm.

M. J. S.

**Modification of Pepys' Gasholder.** By JOSEF HABERMANN and A. OESTERREICHER (*Zeit. anal. Chem.*, 1901, 40, 771).—The water reservoir of the Pepys' gasholder, being smaller than the gas reservoir, requires to be repeatedly filled up with water while the gas is being used, with the result that the gas is subjected to large and sudden

changes of pressure. This inconvenience is altogether obviated by connecting the water reservoir with a side tube having a constant level overflow, such as is commonly used for supplying water-baths.

M. J. S.

**Chemical Balance with Constant Load.** By A. GAWALOWSKI (*Zeit. anal. Chem.*, 1901, 40, 775—776).—The balance has only one stirrup, which carries two scale pans, one above the other. The counterpoise consists of one or more heavy nuts running on a screw which forms an extension of the opposite arm of the beam. To make a weighing, a weight equal to the maximum load for which the balance is constructed is placed on one of the scale pans and equilibrium is adjusted by means of the nuts. The substance to be weighed is then placed on the second pan and equilibrium is restored by altering the weight on the first pan. The difference between the two weights gives the weight of the substance.

M. J. S.

**Simple Apparatus for Drying under Reduced Pressure at High Temperatures.** By FRITZ PREGL (*Zeit. anal. Chem.*, 1901, 40, 781—785).—A glass tube closed at one end is inserted horizontally into an air-bath and a boat containing the substance is pushed into the tube until it occupies a position close to the thermometer. In the portion of the tube external to the oven is placed a boat containing a desiccating agent (calcium chloride, glass beads moistened with sulphuric acid, or phosphoric oxide). The open end of the tube is then closed by a rubber stopper carrying a stop-cock tube and a small mercury manometer. The tube is exhausted and the oven heated. Since the desiccating agent remains cold (which is an essential condition), it exerts its full power of absorbing water vapour, and even substances which are most difficult to dry, reach a constant weight in three to four hours. After admitting dry air to the tube, the boat containing the substance should at once be enclosed in a weighing tube, since even in a desiccator many substances absorb moisture. To protect the tube from being soiled by the desiccating agent, the boat in which this is contained is enclosed in an outer one of thin sheet brass.

M. J. S.

**Apparatus for Extracting Aqueous Liquids by Chloroform.** By FRITZ PREGL (*Zeit. anal. Chem.*, 1901, 40, 785—787).—A glass tube 22 cm. long and 24 mm. in diameter is narrowed at its lower end and joined to a tube 4 mm. in diameter, which is bent upwards parallel to the wide tube. At 2 cm. from the upper end of the wide tube, a side tube 7 mm. in diameter is fused in and is bent downwards and joined to the 4 mm. tube. At the junction, the 7 mm. tube is bent sideways in a nearly horizontal direction for a distance of 16 cm., and then downwards, and at this point is connected with a flask containing chloroform. Chloroform is also placed in the 24 mm. tube, and is then covered with the aqueous liquid to be extracted; an apparatus of this size is constructed to take 50 c.c. A condenser is fitted to the wide tube and the chloroform in the flask is boiled. The vapour rising through the 7 mm. tube is condensed, drips through the

aqueous liquid, and augments the volume of chloroform at the bottom of the 24 mm. tube until this rises to the point where the 4 mm. tube enters that of 7 mm. ; it then flows over into the flask.

M. J. S.

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## Inorganic Chemistry.

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**Lowering of the Freezing Point of Aqueous Hydrogen Peroxide.** By HARRY C. JONES, JAMES BARNES, and EDWARD P. HYDE (*Amer. Chem. J.*, 1902, 27, 22—31. Compare Calvert, this vol., ii, 10).—The molecular lowering of the freezing point of water and aqueous hydrogen peroxide by potassium chloride, sodium nitrate, or potassium nitrate has been determined, and the results show that the salts produce a greater depression in water than in the aqueous peroxide solution. This indicates that the hydrogen peroxide either decreases the dissociating power of the water or that it acts as a polymerising agent. In the case of the potassium nitrate, the smaller depression in the hydrogen peroxide solution cannot be satisfactorily explained by polymerisation, and it is more probable that combination takes place between the salt and the hydrogen peroxide.

The authors recommend the following method of obtaining a pure solution of hydrogen peroxide. Commercial hydrogen peroxide is treated with excess of zinc oxide, and after some time this is filtered off and the solution distilled slowly from a water-bath under a pressure of 60—90 mm. The last two-thirds of the distillate is concentrated on a water-bath at a temperature not higher than 50°.

J. McC.

**Existence of Higher Hydrogen Peroxides.** By A. BACH (*Ber.*, 1902, 35, 158—160. See Abstr., 1900, ii, 470; 1901, ii, 14).—A reply to Ramsay's criticisms (*Trans.*, 1901, 79, 1326). Supplementing the author's previous reply (*loc. cit.*) to Armstrong's criticisms (*Proc.*, 1900, 16, 134), experiments are also described, in which 10 c.c. of a solution of hydrogen peroxide, when titrated with potassium permanganate, is shown to evolve the same quantity of oxygen whether acidified with sulphuric or acetic acid.

R. H. P.

**Preparation of Chlorine from Permanganates.** By CARL GRAEBE (*Ber.*, 1902, 35, 43—45).—The method of preparing chlorine from solid potassium permanganate is preferable to that in which a concentrated solution of the corresponding calcium salt is employed. When concentrated hydrochloric acid is dropped on to the solid potassium salt, the evolution of gas commences at the ordinary temperature; the mixture is finally heated to complete the decomposition of the permanganate, an excess of the acid (10 mols.) being required for this purpose. In this way, a steady current of chlorine free from oxygen or chlorine dioxide is readily obtained.

G. T. M.

**Action of Carbon Dioxide and Alkali Salts on Metallic Oxides, &c.** By O. SACKUR (*Ber.*, 1902, 35, 94—96).—Kühling concludes from his experiments (this vol., ii, 79) that nitric acid is stronger than hydrochloric acid, an exceptional result in view of the parallelism between the strength of an acid and its conductivity and degree of dissociation. The author points out that Kühling's observations are perfectly in accord with well-known physico-chemical laws. The two points in which mercuric nitrate differs from mercuric chloride are (1) the degree of dissociation in solution, which is very small in the case of the chloride, and (2) the tendency to form complex salts, much more marked in the case of the chloride. This difference in the behaviour of mercuric nitrate and chloride has nothing to do with the relative strength of nitric and hydrochloric acids.

J. C. P.

**Relative Strength of Hydrochloric and Nitric Acids.** By GUIDO BODLÄNDER (*Ber.*, 1902, 35, 99—102. Compare Abstr., 1901, ii, 383).—The author criticises Kühling's conclusions (Abstr., 1901, ii, 656, and this vol., ii, 79) that nitric acid is stronger than hydrochloric acid, and shows that Kühling's experiments on the action of carbon dioxide on solutions of alkali chlorides and nitrates in the presence of insoluble metallic oxides are perfectly explicable on the law of mass action and the ionisation theory.

K. J. P. O.

**The Air of the Sea and of Maritime Pine Forests.** By H. DUPHIL (*Soc. sci. et Stat. Zool. d'Arcachon Univ. Bordeaux, Trav. des Lab.*, 1900—1901, 51—67).—The air in the neighbourhood of Arcachon was analysed chemically and bacteriologically. The presence of excess of ozone, of terebenthene, of sodium chloride, and of iodine, and the paucity of bacteria are the main points.

W. D. H.

**Hydrogen Sulphide Apparatus for Students' Laboratories.** By ALFRED WÖHLK (*Zeit. anal. Chem.*, 1902, 41, 14—17).—The principle of the constant apparatus is made use of, with arrangements for drawing off the exhausted acid, and other details which can only be gathered from the figure.

M. J. S.

**Action of Colloidal Platinum on Persulphuric Acid and its Salts.** By T. SLATER PRICE (*Ber.*, 1902, 35, 291—294).—Colloidal platinum does not decompose solutions of potassium or ammonium persulphate, either when neutral or slightly acid; it is also without action on aqueous persulphuric acid obtained by decomposing a solution of its barium salt with sulphuric acid. The speed of decomposition of hydrogen peroxide by platinum is only slightly increased by the addition of persulphates; free persulphuric acid diminishes it. On the other hand, Caro's acid, after dilution with ice, is rapidly reduced by hydrogen peroxide in presence of platinum, although itself not affected by the metal.

The author discriminates between the formulæ  $\text{H}_2\text{SO}_5$  (Baeyer and Villiger) and  $\text{H}_2\text{S}_4\text{O}_{14}$  (Lowry and West) for Caro's acid, in the following way. The formation of the acid  $\text{H}_2\text{SO}_5$ , according to the equations (i)  $\text{K}_2\text{S}_2\text{O}_8 + \text{H}_2\text{SO}_4 = \text{H}_2\text{S}_2\text{O}_8 + \text{K}_2\text{SO}_4$ , (ii)  $\text{H}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} =$

$\text{H}_2\text{SO}_5 + \text{H}_2\text{SO}_4$ , involves the addition to the solution of 1 mol. of an acid for each mol. of Caro's acid formed; the ratio of the amount of iodine measuring the Caro's acid to the growth of acidity (expressed in grams of  $\text{H}_2\text{SO}_4$ ), should thus be 254 : 98, that is, 2.59. Practically it was found to be 2.56. On the other hand, the equations (i)  $2\text{K}_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{SO}_4 = 2\text{H}_2\text{S}_2\text{O}_8 + 2\text{K}_2\text{SO}_4$  and (ii)  $2\text{H}_2\text{S}_2\text{O}_8 = \text{H}_2\text{S}_4\text{O}_{14} + \text{H}_2\text{O}_2$ , predicate the formation of 1 mol. of hydrogen peroxide per mol. of Caro's acid produced, and a value 245 : 34, or 7.17 for the ratio of iodine liberated to the amount of hydrogen peroxide present. The value found for this ratio varied widely, namely, from 136.0 to 566.7; the lack of coincidence with the theoretical value is held to disprove the formula  $\text{H}_2\text{S}_4\text{O}_{14}$  for Caro's acid. W. A. D.

**Presence of Tellurium in American Silver Ingots.** By CAMILLE VINCENT (*Bull. Soc. Chim.*, 1902, [iii], 27, 23—24).—The author finds that the brittleness and bad quality of certain American silver ingots is due to the presence of a small quantity of tellurium. A. F.

**Red Phosphorus.** By RUDOLPH SCHENCK (*Ber.*, 1902, 35, 351—358).—A solution of yellow phosphorus in rectified phosphorus tribromide, when maintained at 170—190°, slowly deposits the red modification, and determinations of the rate of deposition have been made in order to ascertain the nature of the allotropic change. The experiments were carried out in the dark, the solutions being prepared in tubes containing an atmosphere of carbon dioxide. The transformation does not occur in very concentrated solutions, and a concentration of about 1 per cent. was employed.

If red phosphorus is a dimorphous form of the yellow variety, the change would not involve any variation in the number of molecules present and would therefore be unimolecular, having the characteristic differential equation  $-dc/dt = KC$ , where  $C$  is the concentration,  $t$  the time, and  $K$  the transformation velocity constant.

If, however, the red modification is a polymeride of the yellow form, then the reaction is polymolecular and may be represented by the differential equation  $-dC/dt = KC^n$  where  $n$  is the ratio of the molecular complexity of the two allotropes.

The value of  $K$ , found by integrating these equations, would be either  $1/t \log C_0/C$  or  $1/t(n-1)[1/(C^n-1) - 1/(C_0^n-1)]$ , where  $C_0$  is the original concentration. Since red phosphorus is appreciably soluble in phosphorus tribromide, it becomes necessary to modify the preceding expressions by introducing a correction factor  $a$  which represents the amount of the red variety remaining dissolved in the solvent under the conditions of the experiment;  $K$  now becomes either  $1/t(n-1) \log(C_0-a)/(C-a)$  or  $1/t(n-1)[1/(C-a)^{n-1} - 1/(C_0-a)^{n-1}]$ .

The experiments were made at two temperatures, 172° and 184°, and the results, which are tabulated, show that  $K$  is constant only on the assumption that  $n$  is 2, or, in other words, that the reaction is bimolecular.

The addition of a trace of phosphorus tetriodide,  $\text{P}_2\text{I}_4$ , trebles the velocity of transformation without otherwise affecting the character of the change.

The precipitated phosphorus has a bright red colour, and in this

respect corresponds with the variety obtained by Retgers from liquid yellow phosphorus at temperatures below  $250^{\circ}$  and also with that precipitated from the carbon disulphide solution under the influence of light; it is rather more rapidly oxidised than the ordinary dark red commercial product. These differences in colour and chemical behaviour may, however, be due to a finer state of division.

Although the experiments indicate that the initial change is the conversion of  $2P_4$  into  $P_8$ , yet it does not follow that red phosphorus has this molecular complexity; the substance  $P_8$  is probably an extremely labile form rapidly changing into the more highly polymerised final product.

G. T. M.

**Boron Nitride.** By LUDWIG MOESER and W. EIDMANN (*Ber.*, 1902, 35, 535—539).—Boron nitride is best prepared by passing ammonia over a strongly heated and previously fused mixture of boron trioxide and tricalcium phosphate; after washing with dilute hydrochloric acid, an 80—90 per cent. yield of boron nitride is obtained. This is never quite pure, as it is always partially hydrolysed by moist air. When fused with boron nitride, arsenious, antimonious, bismuth, and cadmium oxides are reduced to the metals, with the accompanying formation of borate and nitrous oxide; zinc and ferric oxides are unaltered; molybdenum and chromium trioxides are reduced to lower oxides, and sulphates are reduced to sulphides. A mixture of boron nitride and sodium fluoride, when treated with sulphuric acid, yields ammonium sulphate and boron fluoride. Both sulphur dioxide and carbon dioxide are partially reduced when heated with boron nitride. When melted with sodium peroxide, the nitride yields the nitrate and borate.

R. H. P.

**Use of Potassium Percarbonate as a Substitute for Hydrogen Peroxide.** By FREDERICK P. TREADWELL (*Chem. Zeit.*, 1901, 25, 1008).—Potassium percarbonate is now prepared on the large scale in a high degree of purity, and when in the dry state can be kept without undergoing decomposition. With cold dilute acids, it yields a solution of hydrogen peroxide. It can also be used instead of an alkaline solution of hydrogen dioxide. Thus hydrogen sulphide and soluble sulphides are oxidised to sulphuric acid; manganous, nickel, and cobalt salts to higher oxides, and chromic salts to chromates. Hypochlorites and hypiodites are reduced to chlorides and iodides.

K. J. P. O.

**Preparation and Properties of Sodium Hydride.** By HENRI MOISSAN (*Compt. rend.*, 1902, 134, 71—75).—Sodium hydride,  $NaH$ , is obtained by heating sodium in hydrogen at  $370^{\circ}$ . The regulation of the temperature is important, and the upper part of the tube must be at a slightly lower temperature. It forms white crystals readily decomposed by even a trace of moisture, and taking fire spontaneously if exposed to moist air. When heated in a vacuum, it dissociates at a temperature below the softening point of glass. Its sp. gr. is about 0.92, and it is insoluble in terebenthene, carbon tetrachloride, carbon disulphide, or benzene; it dissolves in fused sodium, and



sodium amalgam, but not in liquefied ammonia. It burns brilliantly in fluorine, or chlorine, or nitrogen peroxide, but not in bromine vapour unless heated; in iodine vapour it ignites at about  $100^{\circ}$ . It also burns when heated in air or oxygen, is decomposed by acids, and, with great energy, by solid oxidising agents. When gently heated in carbon dioxide, it liberates carbon.

C. H. B.

**Solubilities of Mixtures of Sodium Sulphate and Sodium Chloride.** By ATHERTON SEIDELL [with FRANK K. CAMERON] (*Amer. Chem. J.*, 1902, 27, 52—62).—The solubilities of various mixtures of these two salts have been determined at temperatures ranging from  $10^{\circ}$  to  $35^{\circ}$ , and the results are graphically represented by curves. The curves representing the respective quantities of the two salts at  $33^{\circ}$  and higher temperatures consist of two parts with a decided break at a point corresponding with nearly 10 grams of sulphate and about 32 grams of chloride per 100 grams of water. The curves obtained for lower temperatures consist of three parts with two decided breaks. As the quantity of sulphate increases, the first break occurs at practically the same point as that obtained above  $33^{\circ}$ , and the middle part runs parallel with the curve for higher temperatures; then there is a break, and the last part of the curve, representing the solubility of the sulphate in solutions of the chloride of increasing concentration, has a minimum point. The explanation is that above  $33^{\circ}$  the sodium sulphate is anhydrous; below this temperature, the decahydrate is transformed into anhydrous salt in presence of sodium chloride, and therefore the middle part of the curves represent the condition when the solid phase is the anhydrous sulphate. It has been experimentally proved that the transition point of sodium sulphate ( $33^{\circ}$ ) is lowered by the addition of sodium chloride.

J. McC.

**Action of Hydrogen Peroxide on Silver Oxide.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1902, [vii], 25, 78—97).—A detailed account of work already published (compare *Abstr.*, 1901, ii, 383, and this vol., ii, 18).

G. T. M.

**Solubility of Gypsum in Aqueous Solutions of certain Electrolytes.** By FRANK K. CAMERON and ATHERTON SEIDELL (*J. Physical Chem.*, 1901, 5, 643—655).—An extension of the previous work on the solubility of gypsum in sodium chloride solutions (this vol., ii, 75). In magnesium chloride solutions, a maximum solubility was obtained, the concentration of gypsum at this point being about four times that of a saturated aqueous solution. The maximum occurs at about the same chlorine concentration as in the case of sodium chloride solutions. In solutions of calcium chloride, the solubility of gypsum decreases as the concentration of calcium chloride increases, at first rapidly, then slowly. Sodium sulphate causes a decrease of solubility until this attains a concentration of about 17.5 grams per litre, after which it causes an increase. The solubility in sodium chloride solutions, when calcium carbonate was also present in the solid phase, was also investigated; it was found that the presence of the carbonate has

but little effect until the concentration of the sodium chloride reaches about 80 grams per litre, when a sharp, abrupt change of the solubility curve occurs, and the solubility rapidly falls. The author considers the results support the view that ionic complexes are formed in solutions of high concentrations.

L. M. J.

**Solubility of Calcium Hydrogen Phosphate in Water.** By ARTHUR RINDELL (*Compt. rend.*, 1902, 134, 112—114).—Experiments in which different proportions of calcium hydrogen phosphate were agitated in water for times varying from 12 to 252 hours, confirm the author's earlier conclusion that when this salt dissolves in water decomposition takes place, and show that a very considerable time is necessary to establish equilibrium. With quantities of the salt less than 10 grams per litre, saturation is not attained, even after 252 hours. The ratio  $\text{H}_3\text{PO}_4 : \text{CaO}$  has a lower value the less complete the saturation.

C. H. B.

**Preparation and Properties of Strontium Hydride.** By HENRI GAUTIER (*Compt. rend.*, 1902, 134, 100—103).—Strontium hydride,  $\text{SrH}_2$ , is obtained by the action of hydrogen, at an incipient red heat, on the alloy of cadmium and strontium containing 45 per cent. of the latter (this vol., ii, 138). It is a white solid which very readily decomposes water with liberation of hydrogen and development of a large quantity of heat. It is not attacked by chlorine or bromine in the cold, but burns when gently heated in chlorine, and at a dull red heat in bromine vapour. When heated with iodine or sulphur, it is decomposed, and it is violently oxidised when heated with solid oxidising agents. It burns slowly at a red heat in dry air, and more energetically in oxygen.

C. H. B.

**Radioactive Lead.** By FRITZ GIESEL (*Ber.*, 1902, 35, 102—105. Compare Abstr., 1901, ii, 99; this vol., ii, 78).—A specimen of radioactive lead which had retained its activity for a year (*loc. cit.*) has been spectroscopically examined by Demarçay, who finds that in addition to lead (the chief constituent), there are present iron, magnesium, calcium, barium, strontium, chromium, aluminium, manganese, bismuth, and tin, possibly also molybdenum and yttrium. The radium lines are entirely absent, but there are two lines ( $\lambda 3659\cdot6$  and  $\lambda 4116\cdot8$ ) unaccounted for by any of the elements enumerated, and these, along with the radioactivity, might be attributed to some hypothetical substance. It is possible also to regard the radioactivity in question as simply induced in lead by radium; this point is to be further investigated. The author criticises the work and claims of Hofmann and Strauss (Abstr., 1901, ii, 655; this vol., ii, 78).

J. C. P.

**Combination of Sulphates with Hydrogen Chloride.** By CHARLES BASKERVILLE (*J. Amer. Chem. Soc.*, 1901, 23, 894—897) [with LIONEL WEIL].—Mercuric sulphate was treated with strong hydrochloric acid, the mixture evaporated to dryness, and the residue sublimed at  $240^\circ$ ; after washing the sublimate with alcohol and ether, a residue was obtained of a substance,  $\text{HgSO}_4\cdot\text{HCl}$ , which is not affected

by hydrochloric acid and was only slightly soluble in nitric acid. By heating mercuric sulphate in a stream of dry hydrogen chloride, the compound  $\text{HgSO}_4 \cdot 2\text{HCl}$ , described by Ditte (Abstr., 1879, 299; 1880, 12), is obtained. When mercuric chloride is heated with monohydrated sulphuric acid, the compound  $\text{HgSO}_4 \cdot 2\text{HCl} \cdot \text{H}_2\text{O}$  is produced, which sublimes in monoclinic crystals.

[With ISAAC F. HARRIS].—When cadmium sulphate,  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ , is heated at  $150^\circ$ , it loses 4 mols. of water; if it is treated with dry hydrogen chloride at the same temperature, the compound  $3\text{CdSO}_4 \cdot 4\text{H}_2\text{O} \cdot 4\text{HCl}$  is produced, whilst at  $200^\circ$  the compound  $3\text{CdSO}_4 \cdot 8\text{HCl}$  is formed, which on prolonged heating at this temperature or at a dull red heat for a shorter period is converted into cadmium chloride; these new compounds are very deliquescent. E. G.

**Mutual Action of Alumina and Ferric Oxide at Incipient White Heat.** By H. WARTH (*Chem. News*, 1901, 84, 305—306).—When mixtures of alumina and ferric oxide are heated before the blow-pipe, they become pure white in colour provided the proportion of the ferric oxide does not exceed 7 per cent.; beyond that stage, the mixtures are brown after they have been heated. D. A. L.

**Chemical Equilibrium of Carbon-Iron Systems.** By GEORGES CHARPY and LOUIS GRENET (*Compt. rend.*, 1902, 134, 103—105).—The separation of graphite from cast iron is materially influenced by the proportion of silicon, and it is probably neglect of this point which has led to the contradictory results of previous observers. Observations on the behaviour of iron containing different proportions of silicon heated at different temperatures in various ways lead to the following conclusions: the separation of graphite during reheating begins at a lower temperature the higher the proportion of silicon, and when once started will continue at a lower temperature than that at which it begins. At constant temperature, the separation of graphite proceeds progressively at a rate which is lower the lower the temperature and the smaller the proportion of silicon. The proportion of graphite which corresponds with equilibrium is largely independent of the proportion of silicon, but increases as the temperature is lower, so that at low temperatures equilibrium corresponds with the disappearance of all combined carbon; the stable state in the cold coincides with the coexistence of two phases, graphite and pure iron, all the other forms in steel and iron being metastable at a low temperature. C. H. B.

**Oxidation of Ferrous Solutions by Free Oxygen.** By J. W. McBAIN (*J. Physical Chem.*, 1901, 5, 623—638).—Solutions of ferrous salts containing also a known amount of dissolved oxygen were examined after varying time intervals, and the quantity of ferric salt estimated, a colorimetric method being employed. The oxidation was found to be exceedingly slow, but the rate was proportional to the concentration of the oxygen. In ferrous sulphate, the rate of oxidation was approximately proportional to the square of its concentration, but to the cube of the concentration in the case of ferrous acetate, and to the concentration itself in the case of ferrous chloride,

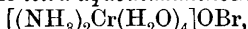
Free acid has a slight retarding effect in the case of the sulphate and acetate, but causes an acceleration in the case of the chloride. The effect of temperature was not fully investigated, but the rate appears to be increased between three- and four-fold for a rise of  $15^{\circ}$ .

L. M. J.

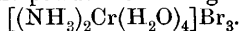
**Action of Potassium Ferricyanide and Soluble Chlorates on Chromium Salts.** By G. SAGET (*Chem. Centr.*, 1902, i, 97; from *Mon. sci.*, 1901, [iv], 15, ii, 764).—Chromium chlorate decomposes on boiling its aqueous solution, chromium trioxide being formed. The addition of potassium ferricyanide facilitates the decomposition. When an aqueous solution of potassium ferricyanide (1 mol.), sodium chlorate (1 mol.), and chromium sulphate (1 mol.) is boiled for an hour, Prussian blue is precipitated, whilst the solution contains chromium trioxide, chlorides, excess of ferricyanide, and a ferric salt; similar reactions take place with other proportions of the salts. Colloidal chromium sesquioxide is also oxidised to chromium trioxide by prolonged boiling with a solution of potassium ferricyanide and sodium chlorate.

E. W. W.

**Tetra-aquodiammino- and Diacidodiaquodiammino-chromium Salts.** By ALFRED WERNER and J. KLIEN (*Ber.*, 1902, 35, 277—291).—Reinecke's salt,  $[(\text{NH}_3)_2\text{Cr}(\text{SCN})_4]\text{NH}_4$ , is oxidised by bromine with complete elimination of the four thiocyno-groups, the latter being thus shown to be combined to the chromium atom through sulphur; the green product is purified by repeatedly precipitating its aqueous solutions with hydrobromic acid, and consists of *dibromodiaquodiamminochromic bromide*,  $[(\text{NH}_3)_2\text{CrBr}_2(\text{H}_2\text{O})_2]\text{Br}$ . The oxidation of  $\alpha$ -trithiocyanodiaquodiamminochromium with bromine yields the same substance, whilst the oxidation of Reinecke's salt with chlorine gives an analogous *chloride*, the product being purified with difficulty. On gradually adding ammonia, or better, pyridine, to an aqueous solution of the bromide, the basic *tetra-aquodiamminochromic bromide*,



is precipitated as a coarsely crystalline, lilac-grey powder; the latter is converted by concentrated hydrobromic acid at  $0^{\circ}$  into a bluish-red, hygroscopic, crystalline powder consisting of the normal *salt*,



*Tetra-aquodiamminochromic chloride*,  $[(\text{NH}_3)_2\text{Cr}(\text{H}_2\text{O})_4]\text{Cl}_3$ , obtained by the action of hydrochloric acid on the basic bromide at  $0^{\circ}$ , is a bluish-pink, crystalline powder, which crystallises from an aqueous solution, concentrated over phosphoric oxide, in bright red, monoclinic prisms; with ammonia, it yields basic *tetra-aquodiamminochromic chloride*,  $[(\text{NH}_3)_2\text{Cr}(\text{H}_2\text{O})_4]\text{OCl}$ , as a bright reddish-violet, crystalline precipitate.

*Tetra-aquodiamminochromic sulphate*,  $[(\text{NH}_3)_2\text{Cr}(\text{H}_2\text{O})_4]_2(\text{SO}_4)_3$ , obtained by adding sulphuric acid to a strongly alcoholic aqueous solution of the basic bromide, forms reddish-violet, hygroscopic leaflets; the basic *sulphate*,  $[(\text{NH}_3)_2\text{Cr}(\text{H}_2\text{O})_4](\text{SO}_4)(\text{OH})$ , formed by the careful addition of ammonia or pyridine, crystallises in slender, red needles and is insoluble in water.

*Tetra-aquodiamminochromic hydroxide*,  $[(\text{NH}_3)_2\text{Cr}(\text{OH}_2)_4](\text{OH})_3\cdot\text{H}_2\text{O}$ ,

obtained from the sulphate by the addition of an excess of ammonia or pyridine, is a violet, crystalline powder.

*Dichlorodiaquodiamminochromium chloride*,  $[(\text{NH}_3)_2\text{CrCl}_2(\text{H}_2\text{O})_2]\text{Cl}$ , is gradually formed when tetra-aquodiamminochromic chloride is kept for some months; it can be purified by precipitating its aqueous solution with concentrated hydrochloric acid, forms bright green leaflets, and contains only one-third of its chlorine in a directly ionisable condition. *Dibromodiaquodiamminochromium bromide* resembles it in all respects.

W. A. D.

**Radioactive Thorium.** By KARL A. HOFMANN and F. ZERBAN (*Ber.*, 1902, 35, 531—533).—The thorium preparations previously described (*Abstr.*, 1901, ii, 19) have lost their radioactivity. The radioactivity of preparations from bröggerite, cleveite, samarskite, &c., can be increased by fractional precipitation with concentrated solutions of potassium sulphate and chromate, hydrogen peroxide, and sodium thio-sulphate, the first portions of the precipitate being the most active, whilst ammonium carbonate precipitates the least active portions. Some thoria prepared from uranium-free monazite was inactive, but this and the older preparations became radioactive after contact for a few days with radioactive uranous oxide. Similar results have been observed by Becquerel (*this vol.*, ii, 117) with radioactive barium.

R. H. P.

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### Mineralogical Chemistry.

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Geocronite from Val di Castello, Tuscany. By GIOVANNI D'ACHIARDI (*Zeit. Kryst. Min.*, 1902, 35, 516—519; from *Atti Soc. Toscana Sci. Nat.*, 1901, Mem., 18, 1—16).—The following mean of four analyses made on material from the same crystal of geocronite gives the formula  $\text{Pb}_5\text{AsSbS}_8$ .

Pb.	As.	Sb.	S.	Total.
70.02	4.47	7.78	17.57	99.84

The results of the crystallographic examination show that geocronite is isomorphous with stephanite ( $\text{Ag}_5\text{SbS}_4$ ); the crystals are twinned, and also possibly hemimorphic, like stephanite :

Geocronite,  $a:b:c = 0.6145:1:0.6797$   
 Stephanite,  $a:b:c = 0.6291:1:0.6851$

A crystallographic relation also exists between geocronite and jordanite ( $\text{Pb}_4\text{As}_2\text{S}_7$ ). L. J. S.

Barytes from the Province Caserta. By PASQUALE FRANCO (*Zeit. Kryst. Min.*, 1902, 35, 523; *Boll. Soc. Geol. Ital.*, 1900, 19, cxxviii—cxxx).—Optical determinations are given of crystals of

colourless, transparent barytes from druses in limestone. Analysis gave:

SO <sub>3</sub> .	BaO.	SrO.	CaO.	Total.	Sp. gr.
34.66	63.33	2.04	trace	100.03	4.333

L. J. S.

**Solubility of certain Natural Silicates in Water.** By GEORGE STEIGER (*Bull. U.S. Geol. Survey*, 1900, No. 167, 159—160).—The experiments of F. W. Clarke on the alkaline reaction of natural silicates (*Abstr.*, 1900, ii, 109) were only qualitative in character: the following quantitative determinations are now made. Half a gram of each of the finely powdered minerals was placed in 50 c.c. of water at about 70° and shaken from time to time. At the end of a month, the filtered solutions were titrated with hydrochloric acid, methyl-orange being used as an indicator. Below are given the percentages of alkalis in each of the minerals, and (in brackets) the percentages of alkalis, calculated as soda, extracted by the water.

Pectolite, 9.11 (0.57); muscovite, 10.00 (0.32); natrolite, 15.79 (0.30); lintonite, 5.92 (0.29); phlogopite, 9.32 (0.22); laumontite, 1.00 (0.18); lepidolite, 13.00 (0.18); elæolite, 21.17 (0.16); heulandite, 2.00 (0.13); orthoclase, 16.00 (0.11); analcite, 14.00 (0.10); oligoclase, 9.18 (0.09); albite, 12.10 (0.07); wernerite, 11.09 (0.07); leucite, 21.39 (0.06); stilbite, 1.00 (0.05); chabazite, 7.10 (0.05). L. J. S.

**Action of Water on Natural Meta-silicates.** By FAUSTO SESTINI (*Zeit. Kryst. Min.*, 1902, 35, 511—512; from *Atti Soc. Toscana Sci. Nat.*, 1900, *Proc. Verb.*, 12, 127—136. Compare preceding abstract).—Distilled water, after remaining in contact with augite for 12—24 hours, acquires a strong alkaline reaction. Augite crystals (280 grams) from Vesuvius, in fragments 1—2 mm. in diameter, were shaken for fifty hours with 750 c.c. of distilled water in a litre flask; there resulted 3.52 grams of a fine powder and 0.161 gram of soluble material, the latter having the composition given under I. When the experiment was repeated in the presence of carbon dioxide, there resulted 3.35 grams of fine powder and 0.2668 gram of soluble material (anal. II). In the second case, the amount of alkalis (Na<sub>2</sub>O and K<sub>2</sub>O) and sulphuric acid is considerably greater than in the first. Blank experiments, however, point to the possibility that some of the dissolved substance is derived from the glass vessels. The fine powder consists of minute fragments of augite and of a white substance soluble in hydrochloric and sulphuric acids, in which the ratio of Al<sub>2</sub>O<sub>3</sub>:Fe<sub>2</sub>O<sub>3</sub> is greater than in the original augite. It follows that augite is decomposed by water at the ordinary temperature with the production of an insoluble aluminium silicate and a soluble portion consisting mainly of an ortho-silicate of calcium, magnesium and ferrous iron; these substances are in turn decomposed by carbon dioxide and oxygen into carbonates, ferric oxide and flocculent silica.

	SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Cl, SO <sub>3</sub> , Alkalis, CO <sub>2</sub> .	
I.	0.0243	0.0043	0.0271	0.0140	gram	traces
II.	0.033	0.0195	0.0246	0.036		"
III.	0.007	0.0018	0.0146	0.0058		—
IV.	0.0068	0.0014	0.0194	0.0160		traces

Diopside (20 grams), treated in the same way in 2 litres of water for 50 hours at  $105^{\circ}$ , yielded 0.0476 gram of soluble substance of which the composition is given under III. Tremolite, in the same amount and under the same conditions ( $105^{\circ}$ ), gave 0.0920 gram of soluble matter (anal. IV). Hornblende, asbestos, and diallage also give an alkaline reaction with water.

L. J. S.

**Mineralogical Notes.** By ARTHUR S. EAKLE, with analyses by W. T. SCHALLER (*Bull. Dept. Geol. Univ. California*, 1901, 2, 315—325).—Pectolite and datolite occur, together with other secondary minerals, as veins in a rock associated with serpentine near San Francisco. The snow-white, fibrous pectolite gave analysis I; the clear, colourless crystals of datolite gave II.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	B <sub>2</sub> O <sub>3</sub> .	CaO.	Na <sub>2</sub> O.	H <sub>2</sub> O (ignition).	Total.
I.	53.40	3.87		—	30.56	7.61	4.46	99.90
II.	36.71	0.17	—	22.11	33.83	—	6.52	99.34

*Esmeraldaite* is the name given to a new hydrous sesquioxide of iron from Esmeralda Co., Nevada. It occurs in earthy limonite as pod-shaped masses of a coal-black colour and with a bright, vitreous lustre. It is glassy, and on the edges translucent with a yellowish-red colour by transmitted light. The streak is yellowish-brown. The mineral is very brittle: H,  $2\frac{1}{2}$ ; sp. gr. 2.578. The mean (III) of several analyses gives, after deducting impurities, the formula  $\text{Fe}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ .

	H <sub>2</sub> O (at $110^{\circ}$ ).	H <sub>2</sub> O (ignition).	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	SiO <sub>2</sub> .	CaO.	P <sub>2</sub> O <sub>5</sub> .	Organic matter.	Total.
III.	15.94	10.24	56.14	5.77	2.05	3.35	4.49	1.37	99.35
IV.	23.72	13.71	12.99	7.44	0.21	—	—	—	

	SO <sub>3</sub> .	FeO.	Na <sub>2</sub> O.	MgO.	
IV.	38.04	0.13	1.68	1.09	99.04

Analysis IV is of a compact, green ferric sulphate, which was taken in a wet, mushy condition from the Redington mercury mine at Knoxville, California. This composition, agreeing with the formula  $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 27\text{H}_2\text{O}$ , suggests coquimbite, in which the iron is partly replaced by aluminium, and in which there is some occluded water, or the substance may be a mixture of coquimbite [ $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ] and alunogen [ $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ].

Crystals of altaite, with the forms {111}, {100}, and {322}, are intimately associated with gold at Sawmill Flat, Tuolumne Co., California; analysis of the crystals gave:

Te.	Pb.	Ag.	Au.	Fe, Se, S.
32.5	65	trace—0.1	nil	traces

Crystals of gold associated with the altaite contain 91.2 to 94.2 per cent. Au.

L. J. S.

**Anorthite from S. Martino, Viterbo.** By FERRUCCIO ZAMBONINI (*Zeit. Kryst. Min.*, 1902, 35, 523; from *Rivista Min. Crist.*, 1900, 24, 4—13).—A crystallographic description is given of crystals of anorthite,



which, with augite, constitute the material of an ejected volcanic block. Analysis gave :

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	CaO.	MgO.	Na <sub>2</sub> O.	Insol.	Total.	Sp. gr.
46.25	34.62	1.20	trace	17.16	0.50	0.95	0.12	100.80	2.78

L. J. S.

**Eclogites of the Aiguilles Rouges.** By ÉTIENNE JOUKOWSKY (*Compt. rend.*, 1901, 133, 1312—1313).—The following analyses are given of minerals isolated from an eclogite in the Mont Blanc district. I, pyroxene; II, uraltitic hornblende; III, garnet.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	Total.
I.	51.28	18.11	—	—	19.17	11.93	100.49
II.	41.24	22.10	—	13.06	12.08	10.31	98.79
III.	37.37	21.52	—	28.32	7.85	5.57	100.43

Some of the hornblende has been produced by the uralitisation of the pyroxene, but that in the kelyphite has been derived by the alteration of garnet.

L. J. S.

**Analyses of Jadeite Axes.** By F. BERWERTH (*Tsch. Min. Mitth.*, 1901, 20, 357—358).—I, jadeite axe found in Hungary; II, in Upper Austria :

	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	SiO <sub>2</sub> .	Total.
I.	22.80	1.83	3.71	trace	15.60	—	(55.48)	100.00
II.	22.76	1.83	1.37	0.95	12.07	1.08	(58.94)	100.00

L. J. S.

**Presence of Jadeite Rocks in the Western Alps and in Liguria.** By S. FRANCHI (*Zeit. Kryst. Min.*, 1902, 35, 521—522; from *Boll. R. Com. Geol. Ital.*, 1900, 31, 119—158; *Atti. R. Accad. Lincei*, 1900, 9, [i], 349—354. Compare Abstr., 1898, ii, 525; 1900, ii, 487).—The author records beyond doubt the occurrence *in situ* of jadeite rocks in the Piedmontese and Ligurian Alps, and establishes the identity of these with the material of the neolithic implements found in the same region, a point before only suggested but not definitely proved. Analysis I is of chloromelanite from Mocchie in the Susa valley, and II of jadeite from Prato Fiorito near Monoiso. The former, sp. gr. 3.33, consists mainly of fibres of pale bluish-green pyroxene, partly altered to smaragdite, and with small amounts of garnet, ilmenite, rutile and pyrites; the latter consists of pyroxene with only very little rutile.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	Na <sub>2</sub> O.
I.	56.85	8.42	9.82	1.12	12.16	4.57	6.91
II.	56.63	17.33	1.74	0.22	13.35	4.36	6.80

	K <sub>2</sub> O.	MnO.	Cr <sub>2</sub> O <sub>3</sub> .	Loss on ignition.	Total.
I.	0.28	trace	—	0.59	100.72
II.	—	—	trace	0.10	100.53

L. J. S.

## Physiological Chemistry.

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**The Respiratory Value of Coelomic Fluid in certain Invertebrates.** By L. CUÉNOT (*Soc. Sci. et Stat. Zool. d'Arcachon Univ. Bordeaux Trav. des Lab.*, 1900—1901, 107—125).—By respiratory value is meant the amount of oxygen which can be obtained from each 100 c.c. of blood or fluid from the body-cavity. In those animals which possess no respiratory pigment, the amount of oxygen is small, in fact the same as in the surrounding water. In those possessing respiratory pigments (hæmocyanin, hæmerythrin, &c.), the value is, as would be anticipated, higher. Analytical details are given.

W. D. H.

**The Blood of the Hippocampus.** By J. SABRAZÈS and L. MURATET (*Soc. Sci. et Stat. Zool. d'Arcachon Univ. Bordeaux Trav. des Lab.*, 1900—1901, 74—80).—The paper is mainly histological. The principal point of interest is the phagocytic action of the leucocytes, which are of the lymphocyte and large mononuclear varieties. Granular leucocytes are absent from the blood of this fish.

W. D. H.

**Coagulation of the Blood of Fishes.** By M. E. RODIER (*Soc. Sci. et Stat. Zool. d'Arcachon Univ. Bordeaux Trav. des Lab.*, 1900—1901, 129—132).—Delezenne has shown that fishes' blood is very slow in coagulating spontaneously, but the phenomenon can be hastened by contact with the tissues. These facts are confirmed in the case of various bony and cartilaginous fishes, and it is also shown that the buccal mucus, and peritoneal fluid of these animals are much more active than pieces of muscular and other tissues in hastening coagulation.

W. D. H.

**Glycolysis in Drawn Blood.** By FREDERICK W. PAVY and R. L. SIAU (*J. Physiol.*, 1902, 27, 451—456).—The loss of sugar which occurs in dog's blood during the first two hours after removal is so insignificant as to be of no physiological importance. This is opposed to Lépine's views, but agrees with those of most other workers on the subject. When the time of exposure is longer (4 to 6 hours), there is a definite but never large loss. It is part of Lépine's doctrine that the larger the amount of sugar present, the larger is the loss. This receives no support from the present experiments, and, as a consequence, the percentage loss will be influenced by the amount of sugar which happens to be present. Lépine's *pouvoir glycolytique* which represents the percentage loss can therefore be made to vary at will.

W. D. H.

**Carbon Monoxide in the Blood. Dissociation of Carboxy-hæmoglobin during Life.** By MAURICE NICLOUX (*Compt. rend. Soc. Biol.*, 1901, 53, 953—955, 955—956. Compare Abstr., 1901, ii, 518, 608).—Previous observations have left it uncertain whether the carbon monoxide of the blood comes from the air, or is produced by

the animal. A few experiments are now recorded which show that the amount of gas in the blood of dogs is doubled in quantity when they live in Paris a few days after having been in the country. The author declines to draw definite conclusions at present.

The hypothesis that a living membrane like the placenta can effect the dissociation of carboxyhæmoglobin, is confirmed by observations on fish. Their blood contains the gas when they are kept in water containing carboxyhæmoglobin, the gill membrane here effecting the dissociation.

W. D. H.

**Calorific and Nutritive Value of Food-stuffs.** By JOHANNES FRENTZEL and NASUJIRO TORIYAMA (*Chem. Centr.*, 1901, ii, 1356; from *Arch. Anat. Physiol. (Physiol. Abth.)*, 1901, 551).—A dog was fed on fat and carbohydrate, and then on the same diet with the addition of meat extract. The calorific value of the excretions rose during the latter period. About 63·5 per cent. of the extract was utilised in the organism.

W. D. H.

**Utilisation of Sugars by the Organism.** By CHARRIN and BROCARD (*Compt. rend.*, 1902, 134, 48—50).—Observations on the appearance of sugar in the urine after ingestion in the stomach lead to the conclusion that from the point of view of utilisation by the economy, lævulose is first, then galactose, and finally dextrose.

W. D. H.

**Digestibility of Food in the Stomach.** By CLAUDIO FERMI (*Chem. Centr.*, 1901, ii, 1355; from *Arch. Anat. Physiol. (Physiol. Abth.)*, 1901, *Suppl. Bd.*, 1—83).—The digestibility of various foods was tested by examining the stomach-contents in animals and men after their ingestion. From these observations and others in which artificial digestion was employed, tables of relative digestibility in the stomach are compiled. In dogs, no salivary digestion goes on in the stomach; this is attributed to want of ptyalin in the dog's saliva. In the same animals, feeding on fat inhibits the formation of hydrochloric acid. The addition of pepsin to a diet of flesh has no influence on digestion.

W. D. H.

**Toxic Substance produced by Gastric Digestion.** By E. CASSART and G. SAUX (*Compt. rend. Soc. Biol.*, 1901, 53, 1072—1074).—A living animal into the circulation of which an artificial gastric digestion of meat is injected dies in convulsions. The toxic material was not identified chemically, but is believed to be identical with that which Brieger termed peptotoxin, and subsequent observers have regarded as an artifact.

The authors consider that such observations can be applied to natural digestion, and will explain such pathological processes as tetany.

W. D. H.

**Bile and Digestion of Proteids.** By SIEGFRIED ROSENBERG (*Chem. Centr.*, 1901, ii, 1355—1356; from *Arch. Anat. Physiol. (Physiol. Abth.)*, 1901, 528—531).—Although bile favours the action of trypsin, Röhmann and

Voit found that with moderate meals of flesh, proteid digestion in the intestine is not impaired by the absence of bile. The same result is noticed when very large amounts of flesh are given. W. D. H.

**The Relation of Lipase to Fat Metabolism.** By A. S. LOEVENHART (*Amer. J. Physiol.*, 1902, 6, 331—360).—The reversible action of lipase will explain fat absorption. Lipase is found in considerable quantities wherever fat synthesis is occurring in the body. 'Lipogenesis' is compared with 'glycogenesis,' its two phases being brought about by the same enzyme, which may be fat-forming or fat-splitting, according to conditions. The fatty changes occurring in phosphorus poisoning are not due to changes in the distribution and amount of lipase in the tissues. W. D. H.

**Lipase in the Lower Animals.** By J. SELLIER (*Soc. Sci. et. Stat. Zool. d'Arcachon Univ. Bordeaux Trav. des Lab.*, 1900—1901, 99—106).—Lipase exists in the blood of the principal types of fishes and of invertebrates. Its activity varies a good deal, even in individuals of the same species. The greatest activity among fishes was found in the conger, the least in the selachians. In invertebrates, lipasic activity does not vary with complexity of organisation, thus it is greater in the worm *Sipunculus* than in the cephalopods. W. D. H.

**The Iron of Lymphatic Glands.** By A. GUILLEMONAT and GABRIEL DELAMARE (*Compt. rend. Soc. Biol.*, 1901, 53, 897—899).—The amount of iron in various lymphatic glands from different animals varies from mere traces to 0.38 per 1000. In inanition, it diminishes; after splenectomy, it increases. These facts point to a hæmopoietic function in lymphatic glands, which is confirmatory of the observations of histologists. W. D. H.

**Adrenalin: the Active Principle of the Suprarenal Glands and its mode of Preparation.** By JOKICHI TAKAMINE (*Amer. J. Pharm.*, 1901, 73, 523—531; *Proc. Physiol. Soc.*, 1901, xxix—xxx).—Adrenalin,  $C_{10}H_{15}O_3N$ , the active principle of the suprarenal glands is isolated, according to the condition of the solutions from which it is crystallised, in the form of prisms, slender needles, rhombic plates, boat or leafed-shaped or nodular crystals. An aqueous solution of adrenalin has an alkaline reaction and rapidly absorbs oxygen from the air, the solution becoming pink, then red, and finally brown in colour. Ferric chloride colours the solution emerald green, whilst iodine imparts a vivid pink. On fusion with potassium hydroxide, two crystalline substances were obtained, probably protocatechuic acid and catechol.

Adrenalin is the strongest hæmostatic agent known and an intra-venous injection produces an enormous rise of blood pressure.

H. R. LE S.

**Formation of Sugar in Boiled Liver.** By FREDERICK W. PAVY and R. L. SIAU (*J. Physiol.*, 1902, 27, 457—458). No sugar is formed in liver substance if it is kept sterile after it is subjected to thorough

boiling. This conclusion harmonises with what general knowledge would suggest, and the experiments were only rendered necessary because persistent statements are often made in text-books to the contrary. W. D. H.

**Post-mortem occurrence of Maltose in the Liver.** By R. LÉPINE and BOULUD (*Compt. rend. Soc. Biol.*, 1901, 53, 1061—1062).—In dogs, even if fed exclusively on meat, maltose is found in the liver some hours after death. The tests relied on are polarimetric, and the preparation of maltosazone. W. D. H.

**Post-mortem occurrence of Glycuronic Acid in the Liver.** By R. LÉPINE and BOULUD (*Compt. rend. Soc. Biol.*, 1901, 53, 1041—1043).—In 12 livers out of 20 (from dogs and guinea-pigs), glycuronic acid is found some hours after death. The same is true for the liver after removal of the pancreas.

The authors rely on polarimetric observations alone for the detection of this substance and its compounds. W. D. H.

**Reticulin and Collagen.** By M. CHRISTINE TEBB (*J. Physiol.*, 1902, 27, 463—472).—Both tendon and reticular tissue consist of fibres which are histologically identical; the main material of which they are composed is collagen. Reticulin, which Siegfried described as characteristic of reticular tissue, does not exist in either form of connective tissue. Siegfried's reticulin is merely collagen which has been 'coagulated' by the reagents he employed (especially alcohol and ether) *plus* proteid and nuclein residues of cells. After treatment with these reagents, conversion into gelatin is rendered much more difficult by subsequent boiling with water. W. D. H.

**The Liberation of a Volatile Sulphide from Milk on Heating.** By LEO F. RETTGER (*Amer. J. Physiol.*, 1902, 6, 450—457).—When milk is heated above 85°, a volatile sulphide, probably hydrogen sulphide, is liberated. The amount, although small, suffices to blacken lead acetate paper and to decolorise dilute solutions of potassium permanganate. Alkalis and alkali phosphates favour, whilst acids and acid phosphates retard, this occurrence. It is believed to indicate proteid decomposition, and to explain what some observers describe as the injurious effects of heating milk. W. D. H.

**The Urine and Kidneys of Fowls fed on Meat.** By FRÉDÉRIC HOUSSAY (*Compt. rend.*, 1901, 133, 1224—1226).—In fowls fed on meat, the amount of urea excreted is increased threefold, as compared with those fed on grain (0.315:0.108). The kidneys are somewhat hypertrophied in the former animals. W. D. H.

**Excretion of Nitrogen during Nervous Excitement.** By FRANCIS G. BENEDICT (*Amer. J. Physiol.*, 1902, 6, 398—410).—Two experiments were made on individuals suffering from excitement due to the witnessing of football matches. In these cases, no noticeable change occurred in nitrogenous metabolism. W. D. H.

**Chromic Acid Diabetes.** By JULIUS KÓSSA (*Pflüger's Archiv*, 1902, 88, 627—637).—Compounds of chromic acid such as potassium chromate, when administered by the mouth or subcutaneously, produce a diabetic condition. This is most intense in dogs; in rabbits, it is not so marked. This condition belongs to the group of 'kidney-diabetes,' and is similar to that produced by phloridzin; the amount of sugar in the blood does not increase. W. D. H.

**Iboga Root and Ibogine.** By LAMBERT and HECKEL (*Compt. rend.*, 1901, 133, 1236—1238).—Subcutaneous injections of ibogine (this vol., i, 114, 174) produces in frogs an abolition of voluntary and reflex movements; the excitability of the muscles and nerves is not altered. Sensation is abolished at the seat of injection. Fairly large doses are necessary to produce death. In mammals, convulsions, and then death from respiratory arrest, occur. The heart is weakened, and this effect is not abolished by section of the vagi. W. D. H.

**Valency, Toxic, and Antitoxic Effects of Ions.** By JACQUES LOEB (*Amer. J. Physiol.*, 1902, 6, 411—433).—A fuller account of experiments already described (this vol., ii, 162). W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Action of Tannins and Colouring Matters on the Activity of Yeasts.** By AUGUSTE ROSENSTIEHL (*Compt. rend.*, 1902, 134, 119—122).—Yeast combines with and withdraws from solution the red colouring matter of grape skins and behaves in the same way with respect to tannin. As a result of this absorption, the fermentative power of the yeast is reduced and finally becomes *nil*, although the power of reproduction may still persist.

The absorptive power of yeast for colouring matters varies considerably; it is *nil* for azo-colours, except those derived from benzidine, and is very feeble for dyes of the phthalein group, but is powerful for dyes of the acridine, thionine, safranine, and rosaniline groups.

C. H. B.

**Occurrence of Methylpentosan in Nature.** By P. RAVN SOLLIED (*Chem. Zeit.*, 1901, 25, 1138—1139).—By means of Tollens and Widstoe's method (*Abstr.*, 1900, i, 244), the author has looked for methylpentosan in the needles and leaves of various trees. A feeble reaction was obtained in the case of *Fucus serratus*, *F. vesiculosus*, *Aseophyllum nodosum*, *Betula odorata*, *Fraxinus excelsior*, *Acer*, *Sorbus Aucuparia*, *Tilia grandifolia*, and *Pinus sylvestris*. Quercitron gave a marked reaction.

K. J. P. O.

**Polygonum Persicaria.** By PAUL HORST (*Chem. Zeit.*, 1901, **25**, 1055—1056).—The leaves of *Polygonum Persicaria* contain water, 10.07 per cent.; ash, 6.52; ethereal oil, 0.053; wax, 1.92; tannin, 1.52; mucin and pectin substances, 5.42; calcium oxalate, 2.18; total nitrogen, 3.97; ammonia, 0.31; cellulose, 27.61; volatile acids, 0.0464, and sugar, 3.24 per cent. The ash, in addition to the usual constituents, is peculiarly rich in manganese. Petroleum extracted a wax which consisted of an ester of phytosterol and oleic acid, together with free phytosterol and free acids from which oleic acid and a solid acid (m. p. 55°) were isolated. The ethereal extract was mainly chlorophyll and a resin. Alcohol extracted sugar, tannin, gallic acid, quercetin,  $C_{15}H_{10}O_7$ , and phlobaphen; the latter, when purified, is a greyish-brown mass, yielding, on hydrolysis with sulphuric acid, a sugar the osazone of which melts at 177—178°. The volatile bases consisted of a mixture of two or three different substances. Volatile acids (acetic and butyric) form the main portion of the ethereal oil, together with two neutral substances, one of which is a camphor-like solid (*persicariol*) with a pleasant odour.

K. J. P. O.

**Yew Wood (*Taxus Baccata*, L.).** By GEORGE THOMS (*Landw.-chem. Versuchs-u. Samen-Control-Station am Polytech. z. Riga*, 1901, Heft 10, 246—250).—The wood contained 89.34 per cent. of dry matter of the following percentage composition: ash, 0.42; C, 50.92; H, 6.33; O, 42.14, and N, 0.19. The crude ash contained 29.6 per cent. of carbon dioxide.

Percentage composition of the pure ash :

K <sub>2</sub> O.	Na <sub>2</sub> O.	CaO.	MgO.	Fe <sub>2</sub> O <sub>3</sub> .	Mn <sub>2</sub> O <sub>4</sub> .	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	SiO <sub>2</sub> .	Cl.
6.24	1.59	68.69	7.39	2.59	0.17	3.36	7.05	1.07	0.55

The large amount of carbon dioxide in the crude ash is probably derived from calcium oxalate in the wood.

N. H. J. M.

**Presence of Sucrose in the Tubercles of *Carum Bulbocastanum*.** By V. HARLAY (*J. Pharm.*, 1902, [vi], **15**, 49—52).—Sucrose has been isolated from the tubercles of *Carum bulbocastanum* (ground-nut), the amount present forming about 10 per cent. of the solid constituents of the tubercles.

H. R. LE S.

**Nutrition of Plants with Phosphorus.** By TH. SCHLÆSING, jun. (*Compt. rend.*, 1902, **134**, 53—55).—The phosphorus soluble in water was determined in two soils in which maize had been grown, and in the same soils without vegetation, but which had been kept moist during the same period. The one soil was comparatively rich in phosphorus soluble in water, the other exceptionally poor. The extraction of soluble phosphorus was repeated ten or eleven times, but was not quite completed. The phosphorus in the maize plants was also determined.

The results showed, in the case of the richer soil, that the soluble phosphorus lost by the soil practically accounted for the whole of the phosphorus in the plants. The plants grown in the poorer soil derived about half their phosphorus from the water-soluble phosphorus of the soil.



The laborious determination of the soluble phosphorus in the soil (Abstr., 1899, ii, 119, 243, and 449) was somewhat shortened by dividing the soils into small portions and extracting them all at the same time.

N. H. J. M.

**Effect of Deficiencies of Potassium, Phosphoric Acid, and Nitrogen on Sugar Production and on the External Form of the Beetroot.** By H. WILFARTH, H. RÖMER, and G. WIMMER (*Zeit. Ver. deut. Zuckerind.*, 1901, 993—1013).—The results of pot experiments with sugar beet showed that the absence of potassium, phosphoric acid, and nitrogen each produced characteristic effects on the leaves of the plants. In each case, the roots remained very small.

Sugar production is very slight when potassium is very deficient, and if at the same time, much nitrogen is supplied, the amount of sucrose will be almost nothing and the roots have a great tendency to decompose. The leaf production is comparatively large in absence of potash and essentially greater than when phosphoric acid and nitrogen are absent.

In absence of phosphoric acid, the roots, although small, are quite healthy and fairly rich in sugar as compared with roots grown without potassium. With a deficiency of phosphoric acid which reduces the weight of the roots to 13·8 grams, the amount of sugar is as high as 14 per cent.

When nitrogen is deficient, healthy roots with much sugar are produced. Roots weighing only 15 grams may contain 17·8 per cent. of sugar.

N. H. J. M.

**Studies in the Chemical Analysis of Fresh and Salt Waters. Part I. Applications of the Aëration Method of Analysis to the Study of River Waters.** By WALTER E. ADENEY (*Sci. Proc. Roy. Dublin Soc.*, 1900, 9, 346—361).—The advantages of the author's aëration method of analysis (Abstr., 1896, ii, 322) are pointed out, and the conclusions that may be deduced from it are illustrated by a detailed examination of three waters: (1) a slightly polluted non-tidal water; (2) a potable water; (3) a tidal water. Stress is laid on the necessity of determining in a water, not only the dissolved oxygen, but all the dissolved gases.

J. C. P.

**Nature and Speed of the Chemical Changes which occur in Mixtures of Sewage and Sea Water.** By EDMUND A. LETTS, ROBERT F. BLAKE, W. CALDWELL, and J. HAWTHORNE (*Sci. Proc. Roy. Dublin Soc.*, 1900, 9, 333—345).—An investigation of a preliminary character. Mixtures of sewage and sea-water were kept in closed vessels for a number of days, and the quantity of the various dissolved gases determined at intervals. It seems that the first chemical change is the absorption of oxygen and the production of almost the equivalent quantity of carbon dioxide. A comparison of the analyses of the dissolved gases and the amount of 'oxygen absorbed' as given by the permanganate test shows that a more energetic oxidation is effected by micro-organisms and free oxygen than by the permanganate solution. Free and albuminoid ammonia, nitrates, and nitrites were

determined at the same intervals, and it appears that in the earlier stages of the fermentative process, interchanges took place between the free and the albuminoid ammonia.

Mixtures of sewage and sea-water were kept also in open vessels, and the changes studied in a similar fashion, but the experimental data are not yet numerous enough to warrant any general conclusions.

J. C. P.

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## Analytical Chemistry.

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**The Employment and Sensibility of Litmus Extract.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1902, [vii], 25, 39—53).—Litmus extract gives definite end points with acids, the heats of neutralisation of which lie between 13.6 and 16 Cal., this being the value obtained for each hydrogen ion neutralised in dilute solution. The end point is, however, indeterminate in the case of those acids in which this constant is approximately 11—12 Cal., and, moreover, it varies with the degree of dilution. The behaviour of litmus employed as an indicator under various conditions is fully discussed, but the remainder of the communication is not suitable for abstraction (compare Abstr., 1901, ii, 502, 551). G. T. M.

**Indicators.** By F. GLASER (*Zeit. anal. Chem.*, 1902, 41, 36—42).—To the strictures of J. Wagner (Abstr., 1901, ii, 419) on the author's classification of indicators, it is replied that it was intended for practical purposes, and to Wagner's proposed classification according to the mode of their ionisation, it is objected that the constitution of many indicators is at present unknown, that many coloured substances of essentially different chemical constitution have an equal practical efficiency as indicators, and that Wagner's classification groups together indicators which behave very differently in actual use. Wagner's conclusions with regard to Congo-red seem to be due to an error in the work of Schimansky (Abstr., 1900, i, 305). The blue substance precipitated by adding hydrochloric acid to Congo-red does not contain chlorine, neither does it change in colour by exhaustive washing in a platinum vessel. If, however, transferred to a glass vessel, it dissolves with red colour in consequence of the solution of alkali from the glass. M. J. S.

**Gravimetric Method for the Estimation of Hydrogen Peroxide.** By GEORGE E. HOSCH (*J. Amer. Chem. Soc.*, 1901, 23, 923—924).—The drying tube of a Schrötter's apparatus (as employed for the estimation of carbonates) is half filled with concentrated sulphuric acid, the 'acid tube' with a 2 per cent. solution of potassium permanganate, and in the bulb are placed 10 c.c. of water and 5 c.c. of dilute sulphuric acid (1:5). The weight of the apparatus is noted both before and after the addition of about 1 c.c. of the hydrogen

peroxide solution. The permanganate is allowed to enter drop by drop until a permanent coloration is produced. The apparatus is allowed to cool, and is then weighed. One-half of the loss in weight is due to oxygen of the hydrogen peroxide. E. G.

**Estimation of Sulphur in Proteids.** By THOMAS B. OSBORNE (*Zeit. anal. Chem.*, 1902, 41, 25—35).—See this vol., i, 250.

**Estimation of Small Amounts of Hydrogen Sulphide in Natural Waters.** By LUDWIG W. WINKLER (*Zeit. anal. Chem.*, 1901, 40, 772—774).—When the amount of hydrogen sulphide is extremely small, the Dupasquier-Fresenius method is useless, and in such cases, a colorimetric method may be employed. The solutions required are: (1) 25 grams of sodium potassium tartrate, 5 grams of sodium hydroxide, and 1 gram of lead acetate made up to 100 c.c. (2) 0.0367 gram of arsenic trisulphide dissolved in ammonia and made up to 100 c.c., each c.c. of this solution corresponds with 0.1 c.c. of hydrogen sulphide at 0° and 760 mm. The solution must be freshly made.

A measured quantity of the natural water is mixed with about 5 per cent. of reagent (1), and the depth of colour is matched by adding reagent (2) from a burette to a similar mixture of reagent (1) with distilled water. M J. S.

**Estimation of Free Sulphuric Acid in Leather.** By J. PAESSLER and H. SLUYTER (*Chem. Centr.*, 1902, i, 137—138; from *Bull. assoc. belge Chimistes*, 15, 313—321).—A criticism of the methods proposed by Balland and Maljean (*Abstr.*, 1896, ii, 499), Jean (*Rev. intern. falsific.*, 8, 188), Procter and Searle (*Leather Trades Rev.*, 1901) and Schroeder.

The first method suffers from the defect that the natural sulphur of the leather is disregarded; this may be remedied by deducting 0.14 per cent. from the sulphur trioxide found. It must be remembered that in this method some normal sulphates such as those of iron, aluminium, and chromium lose their sulphuric acid on ignition, and this loss should be allowed for when calculating the amount of free acid.

Jean's process gives too low results, as leather retains free acids which cannot be removed by solvents.

Procter and Searle's method is based on the same principle as Hehner's process for the estimation of mineral acids in vinegar. The authors state that the alkalinity of the ash from another piece of the sample should always be determined and allowed for. With some kinds of leather, the method gave negative results from some unexplained cause.

In Schroeder's process, the sulphuric acid and sulphates are extracted with 1 per cent. hydrochloric acid. The authors found that pure water scarcely extracts the acid. L. DE K.

**Gasometric Estimation of Sulphates and Carbonates.** By E. RIEGLER (*Zeit. anal. Chem.*, 1902, 41, 17—25).—Barium chloride, when treated with iodic acid, forms barium iodate, and the latter, when treated with hydrazine sulphate, evolves nitrogen according to the equation  $\text{Ba}(\text{IO}_3)_2 + 3\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4 = \text{BaSO}_4 + 2\text{H}_2\text{SO}_4 + 2\text{HI} + 6\text{H}_2\text{O} + 3\text{N}_2$ . The

slightly acidified solution of the sulphate (30—40 c.c.) is treated with an excess of barium chloride (30.5 grams of the crystallised salt in a litre), taking care that the excess does not exceed 5 c.c. The mixture is boiled and allowed to cool; there is then added 5 c.c. of a 6 per cent. solution of iodic acid, and after 15 minutes the mixed precipitate is collected on a small filter and washed until the total filtrate amounts to 100 c.c. The filter with its contents is then placed in the reaction flask of a Knop-Wagner azotometer and treated in the usual way with 40 c.c. of a 2 per cent. solution of hydrazine sulphate. The reaction is complete when the contents of the flask become colourless. The nitrogen is calculated into  $\text{SO}_3$  (by a table which is supplied); a correction of 3.5 mg. is added for the solubility of barium iodate (22.4 mg. in 100 c.c.) and the amount is deducted from 10 times the number of c.c. of barium chloride employed.

For estimating carbonates, the carbonic acid is precipitated by barium hydroxide; the precipitate is well washed, dissolved in a small excess of hydrochloric acid, and the barium chloride treated as just described. The correction for solubility is in this case 2.1 mg. of carbon dioxide.

M. J. S.

**Estimation of Nitrogen.** By E. DURAND (*Ann. Chim. anal.*, 1902, 7, 17—18).—The author recommends the apparatus formerly used by Kjeldahl, which does not seem to be generally known. It consists of a distilling flask of 800 c.c. capacity, made out of a single piece of copper. The flask is connected with the condenser by means of a Kjeldahl-Stutzer bulb apparatus.

When using this copper distilling flask, it is as well to avoid the introduction of mercurial compounds, and the conversion of the nitrogen into ammonia should be effected by means of sulphuric acid and a little copper oxide (compare Jean, this vol., ii, 172).

L. DE K.

**Mitscherlich's Test for Phosphorus in presence of Alcohol.** By JOSEF HABERMANN and A. OESTERREICHER (*Zeit. anal. Chem.*, 1901, 40, 761—766).—It is well known that the phosphorescent luminosity, which in Mitscherlich's test is the characteristic evidence of the presence of free phosphorus, is prevented by the presence of many volatile organic substances, of which alcohol is the one most likely to be present in a chemico-toxicological examination. If the quantity of phosphorus present is very small compared with the alcohol, it may be impossible to distil off the alcohol without the whole of the phosphorus passing over also, in which case the luminosity may be entirely prevented. The authors, however, find that by adding water to the distillate, the disturbing effect of alcohol may be to a great extent eliminated. A better plan is to insert the jet of a stop-cock funnel into the upper end of the Liebig's condenser, and to allow cold water to drop from the funnel during the distillation. A luminous band will then be observed in the condenser. If the liquid under examination contains more than 50 vols. per cent. of alcohol, even this method fails, but by adding water to the contents of the distillation flask prior to distilling, the luminosity will be observed even when the original liquid consisted of absolute alcohol.

M. J. S.

**Behaviour of Calcium Hypophosphite in the Animal System.** By THEODOR PANZER (*Zeit. Nahr. Genussm.*, 1902, 5, 11—14).—Experiments with dogs showed that calcium hypophosphite is rapidly eliminated from the system and passes unaltered into the urine. The presence of hypophosphite may be generally detected after half-an-hour, and no more can be found after 24 hours. The other organs, blood, and faeces are practically free from hypophosphite. In human beings the elimination seems to take a little longer.

In case of a supposed poisoning by phosphorus, enquiries should be made as to whether the person has taken any hypophosphite shortly before death; should this be proved, the presence of phosphorous acid in the urine or intestinal canal counts for nothing. L. DE K.

**Estimation of Phosphoric Acid in Organic Substances.** By FRITZ RIEGER (*Zeit. physiol. Chem.*, 1901, 34, 109—113).—The method consists in evaporating the substance, for example, milk, to a syrup in a platinum dish, then heating with a relatively large amount of finely divided sodium carbonate, and finally with sodium carbonate and potassium nitrate. The fused mass is dissolved in nitric acid, and the phosphoric acid precipitated by ammonium molybdate in the usual manner. A modified Keller's method (*ibid.*, 1900, 29, 150) has also given good results.

A third method consists in precipitating the proteids in milk by the aid of copper sulphate and sodium hydroxide (Ritthausen, this Journal, 1877, ii, 519), and estimating the phosphorus in this precipitate by fusion with sodium carbonate and potassium nitrate. J. J. S.

**Detection of Traces of Arsenic in Articles of Food.** By J. C. BERNTRUP (*Zeit. anal. Chem.*, 1902, 41, 11—13).—The arsenic is converted into arsenic acid by adding bromine; sodium phosphate and magnesia mixture are then added. The precipitate of magnesium ammonium phosphate carries down the magnesium ammonium arsenate. The precipitate is washed with ammonia, dissolved from the filter by dilute sulphuric acid, and the solution evaporated with addition of nitric acid until fumes of sulphuric acid begin to volatilise. All organic matter is thus got rid of; the solution is fit for either Marsh's or Gutzeit's test, and there is no danger of interference from antimony if originally present. M. J. S.

**Boric Acid.** By K. FARNSTEINER (*Zeit. Nahr. Genussm.*, 1902, 5, 1—8).—Instead of using dilute glycerol as a solvent, the author has successfully estimated boric acid by dissolving it in absolute methyl alcohol and titrating with  $N/2$  solution of potassium, sodium, or barium hydroxide (also dissolved in absolute methyl alcohol), using phenolphthalein as indicator. It is necessary to continue the titration until the end reaction is very marked, as a very slight pink will show before the reaction is quite finished. The solution may be titrated after being kept for 24 hours. The distillate obtained by heating boric acid with methyl alcohol, which is supposed to contain methyl borate may be titrated almost as readily as if it were a solution of boric acid.

If crystallised borax is titrated in this manner, half of its boric

acid is practically obtained; the results are a trifle too low, no doubt owing to the hydrolysing influence of the water of crystallisation.

Absolute ethyl alcohol cannot be substituted for methyl alcohol, as the end reaction is then reached when only one-sixth or one-seventh of the acid has been converted into the normal salt. On using 95 per cent. alcohol, results are obtained in which the proportion of boric acid and alkali varies from about 2.36, 2.18, or 2 to 1, instead of showing the normal proportion 1 to 1. No satisfactory explanation can as yet be given.

L. DE K.

**Some Problems connected with Atmospheric Carbon Dioxide, and a New and Accurate Method for Estimating its Amount Suitable for Scientific Expeditions.** By EDMUND A. LETTS and ROBERT F. BLAKE (*Sci. Proc. Roy. Dublin Soc.*, 1901, 9, 436—453. Compare Abstr., 1900, ii, 622).—In the authors' opinion, the study of the variation of the amount of atmospheric carbon dioxide under varying conditions of wind, weather &c., especially above the ocean, is of great importance. Accordingly, a method of estimating the carbon dioxide of the atmosphere is here described, which involves only comparatively simple operations at the place of observation. The method resembles Pettenkofer's in that a relatively small volume of air is examined, but a dilute (approximately  $N/40$ ) solution of potash is used to absorb the carbon dioxide, which is afterwards liberated by treatment with acid and measured; the latter part of the process is carried out with Adeney's apparatus (*Trans. Roy. Dublin Soc.*, 1895, [ii], 5, 548), which is found to give very accurate results. The authors describe and sketch the apparatus used for transferring an accurately measured quantity of the absorbent into the receiver containing the air to be examined, the absorbent being all the time out of contact with the external atmosphere. The correction necessary for any carbon dioxide already present in the absorbent is determined by a blank experiment. The authors have tested their method by using artificial mixtures of pure air and carbon dioxide; the mean error in their experiments is 0.04 part per 10,000 of air, and the method is therefore accurate enough to determine the fluctuations in the amount of atmospheric carbon dioxide.

A modification of the process, suitable for field work or for scientific expeditions, is also proposed, in which sealed tubes, each containing 50 c.c. of the weak potash solution, are prepared beforehand. When a tube is to be used, its ends are broken and, by suitable means, the contained solution is brought into contact with the air to be examined; after the absorption is complete, the solution is re-introduced into the tube, the latter is sealed again, and its contents may be examined subsequently.

J. C. P.

**Estimation of Sodium and Potassium in Urine.** By G. C. GARRATT (*J. Physiol.*, 1902, 27, 507—510).—A slight modification of Lehmann's method is proposed, and also a simpler method, which gives nearly accurate results.

W. D. H.

**Relations of Absorption to Analytical and Agricultural Chemistry.** By ROBERT SCHALLER (*Zeit. angew. Chem.*, 1901, 14, 1294—1296).—The results of estimations of calcium in soil extracts

after precipitating the iron with ammonia, showed in some cases that more than half the calcium is lost owing to its being absorbed by the ferric hydroxide. It is shown that the absorption of calcium increases with the concentration, but that relatively less is lost in strong than in weak solutions. The loss of calcium also increases with the amount of iron in solutions containing the same amount of calcium.

Mechanical absorption by ferric hydroxide also occurred in the case of magnesium hydroxide and potassium dichromate. N. H. J. M.

**Report of the American Sub-Committee on Uniformity in Analysis of Materials for the Portland Cement Industry.** [CLIFFORD RICHARDSON, SPENCER B. NEWBERRY, and H. A. SCHAFER] (*J. Soc. Chem. Ind.*, 1902, 21, 12—30).—The committee has examined 18 different schemes for the analysis of Portland cement, and recommends the following tentative method: 0.5 gram of the finely powdered material is strongly ignited in a platinum crucible for 15 minutes, transferred to a platinum dish, and treated with 50 c.c. of water and 10 c.c. of hydrochloric acid; the whole is finally evaporated as nearly as possible to dryness on a water-bath. *Silica.* The residue is treated with 5—10 c.c. of strong hydrochloric acid, and, after adding water, the whole is heated for 10 minutes on the water-bath, and the silica collected on a filter and washed. The filtrate is again evaporated to dryness and the residue taken up with acidified water, when the small amount of additional silica is again collected. The two filters containing silica are then transferred while moist to a platinum crucible and gradually heated, finally over a blowpipe, until constant weight is obtained. The purity of the silica may be tested as usual with hydrofluoric acid. *Aluminium and ferric oxides.* The filtrate from the silica is made alkaline with ammonia, well boiled, and the precipitate collected and washed, once by decantation and slightly on the filter. It is then dissolved in hydrochloric acid and reprecipitated by ammonia and the precipitate is ignited and weighed. *Ferric oxide.* The precipitate is fused with potassium hydrogen sulphate, the fused mass dissolved in hot water and 25 c.c. of dilute sulphuric acid. The small amount of silica is collected and weighed. The filtrate is treated with hydrogen sulphide, the excess of this boiled off whilst a current of carbon dioxide is passed, and the ferrous iron then titrated with permanganate. *Calcium oxide.* To the filtrate from the aluminium and iron are added a few drops of ammonia, the solution is boiled, and 10 c.c. of a saturated solution of ammonium oxalate are added. The precipitate is collected and placed while moist in a platinum crucible, when it is gradually ignited. The ash is redissolved in a little hydrochloric acid and diluted with water to about 100 c.c., ammonia is added in slight excess and the liquid boiled and reprecipitated with ammonia oxalate. If the ammonia should produce a slight precipitate of alumina, this should be collected and weighed. The calcium oxalate, now pure, is titrated with permanganate or else converted into oxide by ignition over the blast and weighed. *Magnesium oxide.* The filtrates from the calcium are acidified with hydrochloric acid, concentrated to about 150 c.c., and mixed with 30 c.c. of a saturated solution of microcosmic salt; the whole is then boiled for a few minutes. When cold, ammonia is slowly



added while stirring until the crystalline precipitate begins to form ; a slight excess of ammonia is then added, and the stirring continued for a few minutes. After a few hours, the precipitate is collected, re-dissolved in hot dilute hydrochloric acid, diluted to 100 c.c., mixed with 2 c.c. of phosphate solution, and again precipitated by ammonia as before. After two hours, it is collected, ignited, and weighed. *Alkalis.* The sample is heated as usual with ammonium chloride, but there is no need to add calcium carbonate. *Sulphur trioxide.* One gram of the sample is dissolved in 15 c.c. of hydrochloric acid, and the solution diluted with water and filtered. Without troubling about the dissolved silica, the solution is heated to boiling and mixed, drop by drop, with 10 c.c. of a saturated solution of barium chloride. The barium sulphate is collected and weighed. *Total sulphur.* One gram of the sample is similarly treated after a preliminary fusion with sodium carbonate and a little potassium nitrate, avoiding contact with sulphurous gases. *Loss on ignition.* 0.5 gram of the sample is heated for 15 minutes over the blowpipe and weighed ; the loss in weight is checked by another 5 minutes' ignition.

If the sample should not entirely dissolve in hydrochloric acid, the insoluble matter should be collected and rendered soluble by a preliminary fusion with sodium carbonate. The aluminium-iron precipitate may contain also traces of titanium, manganese, and phosphoric oxides.  
L. DE K.

**Microchemical Test for Magnesium.** By M. E. Pozzi-Escot (*Ann. Chim. anal.*, 1902, 7, 10—11).—A reply to several criticisms. When dealing with extremely dilute solutions, the addition of ammonia to the mixture of magnesium salt, ammonium chloride, and sodium phosphate is advantageous, and a crystalline deposit will be obtained.  
L. DE K.

**Analysis of Crude Copper and Mattes. Part I.** By P. TRUCHOT (*Ann. Chim. anal.*, 1902, 7, 1—5. Compare Abstr., 1900, ii, 197).—The copper borings or filings are freed from any adhering particles of metallic iron by means of a magnet and, if greasy, washed with ether. Mattes are reduced to powder and passed through a No. 100 sieve. Any coarse particles of metallic copper are collected, weighed, and analysed separately ; they only occur in blue or bronze, but not in white mattes. Ten grams of black copper or mattes are treated with a mixture of 50 c.c. of nitric acid of sp. gr. 1.3 and 10 c.c. of sulphuric acid of sp. gr. 1.6, and sufficient water is added to moderate the violence of the reaction. When the action has ceased, any particles of unoxidised sulphur are dissolved by adding a few c.c. of bromine. After adding 5 c.c. of sulphuric acid, the liquid is evaporated until sulphuric acid fumes have practically ceased ; the residue is dissolved in dilute sulphuric acid and the undissolved portion, consisting of oxides of tin and antimony, lead sulphate, &c., washed with water to which a few drops of sulphuric acid have been added.

*Estimation of lead.* The insoluble matter is digested with 25 c.c. of a saturated solution of ammonium acetate. To the filtrate are added

40—50 c.c. of nitric acid and sufficient water to bring the volume up to 300 c.c.; the solution is submitted to electrolysis, using a current of 0.2 ampere and 2.5 volts, which causes the lead to precipitate as dioxide; this is then washed, dried at 180°, and weighed. In this and subsequent electrolyses, the surface of the anode, or cathode, has always been 80 decimetres square.

*Estimation of copper.* The original solution is mixed with 10—15 c.c. of nitric acid, diluted to 300 c.c., and electrolysed, using a current of 0.4 ampere and 2.5 volts; the operation, which takes about a day and a half, may be accelerated by using at first a current of 1.5 amperes. From the weight of the copper thus obtained, any silver afterwards found must be deducted. The liquid is now evaporated on a sand-bath until the sulphuric acid is completely expelled, the residue dissolved in hot dilute hydrochloric acid, and after heating at 80° to 85°, freed from any arsenic, antimony, tin, bismuth, &c., by a current of hydrogen sulphide. The filtrate is boiled and fully oxidised by a few drops of bromine, the excess of which is expelled by boiling a little longer. *Estimation of iron.* The liquid is neutralised with sodium carbonate and the iron precipitated by adding 10—20 grams of sodium acetate and boiling. The precipitate is redissolved and reprecipitated, and then purified a third time by reprecipitation with ammonia. It is finally dissolved in dilute sulphuric acid and titrated with permanganate. *Estimation of zinc.* The united filtrates from the iron are evaporated with hydrochloric acid, the chlorides are dissolved in water, and mixed with sodium carbonate until a slight precipitate has formed, which is redissolved by adding 1 or 2 drops of hydrochloric acid. A current of hydrogen sulphide is passed and a few drops of a very weak solution of sodium acetate are added. The precipitated zinc sulphide is freed from traces of cobalt and nickel by boiling with dilute hydrochloric acid and finally adding an excess of sodium hydroxide, which dissolves the zinc oxide and leaves cobalt and nickel oxides undissolved. The zinc is then deposited on platinum coated with copper by electrolysis, using a current of 0.4 ampere and 3 volts. *Estimation of manganese.* The filtrate from the zinc is boiled to expel hydrogen sulphide and then mixed with the solution obtained on dissolving the nickel and cobalt oxides, which are recovered from the zinc sulphide, in hydrochloric acid. The manganese is precipitated by adding ammonium phosphate and excess of ammonia. The manganous ammonium phosphate is washed with dilute ammonia, redissolved in hydrochloric acid, and afterwards titrated in the usual manner with permanganate. *Estimation of nickel and cobalt.* The filtrate from the manganese is submitted to electrolysis, using a current of 0.5 ampere and 3 volts; this gives the joint amount of nickel and cobalt. The latter is then separated by the potassium nitrite method and finally electrolysed in the presence of ammonium phosphate and ammonia. *Estimation of arsenic and antimony.* The author uses Hollard's method (Abstr., 1900, ii, 442).

L. DE K.

**Estimation of Copper in Pyrites.** By HERBERT HAAS (*Zeit. anal. Chem.*, 1901, 40, 789).—With reference to Heidenreich's method (Abstr., 1901, ii, 197), the author objects that electrolytic precipitation

does not fulfil the condition of rapidity which is essential in a copper works. By dissolving the precipitated copper in nitric acid and titrating with cyanide, identical results are obtained and more rapidly.

M. J. S.

**Solubility of Copper Sulphide in Alkali Sulphides: Separation of Copper, Lead, Antimony, and Tin.** By ADELBERT RÖSSING (*Zeit. anal. Chem.*, 1902, 41, 1--11).—The common practice of employing sodium polysulphide, either in the dry or wet way, for the separation of copper and lead from antimony and tin, leads to errors, since copper sulphide is appreciably soluble in alkali polysulphides. In sodium monosulphide, copper sulphide is practically insoluble, but since stannous sulphide is not soluble in that reagent, it is necessary that all the tin should be in the stannic condition. The method of separating antimony and tin from lead and copper, in analysing alloys, by oxidation with nitric acid, cannot be recommended, as both the latter metals are invariably found in the insoluble residue. If, however, the residue left after evaporating the nitric acid is at once treated with colourless sodium sulphide (after ensuring the absence of acid by adding a little sodium hydroxide) a complete separation can be effected. A more rapid method is to dissolve the alloy (2 grams) in a little nitrohydrochloric acid, warm the solution with potassium chlorate, dilute with water containing tartaric acid, make feebly alkaline with sodium hydroxide, and add colourless sodium sulphide in the smallest possible excess. For separating the antimony and tin in the filtrate, a modification of Clark's method is advisable. The solution is decolorised by hydrogen peroxide, nearly neutralised with hydrochloric acid, mixed with 25—30 grams of oxalic acid, and treated for half-an-hour with hydrogen sulphide. It is well to dissolve the precipitated antimony sulphide once more in sodium sulphide and repeat the precipitation after adding 15—20 grams of oxalic acid, as traces of tin are present in the first precipitate. The filtrate is then made alkaline with ammonia, ammonium sulphide added, and the stannic sulphide thrown down by acetic acid. Hydrogen sulphide should be passed, as a considerable excess is necessary to ensure the complete precipitation of the tin. The antimony sulphide should be freed from sulphur by treatment with a mixture of alcohol and carbon disulphide, removed completely from the filter, and heated with fuming nitric acid until the last traces of sulphur are oxidised, since the ignition of antimony tetroxide with sulphur invariably causes loss.

M. J. S.

**Estimation of Molybdic Acid reduced by Hydriodic Acid.** By FRANK A. GOOCH and O. S. PULMAN, jun. (*Amer. J. Sci.*, 1901, [iv], 12, 449—451).—0.3—0.5 gram of the molybdate compound is boiled with 40—60 c.c. of hydrochloric acid of sp. gr. 1.2 containing 0.2—0.6 gram of potassium iodide in a 150 c.c. flask trapped loosely by means of a short bulb tube hung in the neck. The boiling is continued until the volume of the liquid is reduced to exactly 25 c.c.; it is diluted with cold water to 125 c.c. and transferred to a Drexel wash-bottle fitted with a ground glass stopper carrying the usual inlet and outlet tubes. To the inlet tube is sealed a separating funnel for the gradual

introduction of reagents, and to the outlet tube a Will and Varrentrap bulb apparatus containing solution of potassium iodide to prevent any mechanical loss of iodine during the subsequent neutralisation. Through the funnel is added a solution of 0.5 gram of manganous sulphate, and from a burette a  $N/10$  solution of potassium permanganate until the solution assumes the characteristic colour. From a burette is then added a quantity of standard solution of sodium arsenite corresponding in strength with the permanganate used. To prevent precipitation of molybdic oxide on neutralising, a solution of 3 grams of tartaric acid is added and the acids are then neutralised with potassium hydrogen carbonate. The liquid adhering to the stopper and tubes and also the contents of the bulbs are rinsed into the bottle and the residual arsenite is titrated with standard iodine, using starch as indicator. The theory of the process is plain: the value in terms of molybdic acid of the permanganate used, diminished by that of the arsenite and increased by that of the iodine, gives the amount of molybdic acid present. L. DE K.

**Titration with Stannous Chloride.** By FRÉDÉRIC WEIL (*Compt. rend.*, 1902, 115).—Titrations with stannous chloride can be accurately carried out at the ordinary temperature if the liquid is mixed with an excess of hydrochloric acid and some fragments of white marble are added so that the vessel becomes filled with carbon dioxide. C. H. B.

[**Estimation of Vanadium.**] By H. PROCTER SMITH (*J. Soc. Chem. Ind.*, 1902, 21, 1183—1188).—*Estimation of Vanadium in Ores containing Lead, Copper, Iron, &c.*—A quantity of the sample containing about 0.05 gram of vanadium is dissolved in a little hydrochloric acid, the solution is diluted to 250 c.c. and treated with hydrogen sulphide. The liquid is filtered, and the precipitate redissolved in a little nitric acid; the bulk of the acid is expelled by evaporation, and after dilution with water the solution is again treated with hydrogen sulphide. The two filtrates are mixed and evaporated to dryness in a platinum crucible; the residue contains the vanadium and the iron. It is then fused with an excess of a mixture of 2 parts of dry sodium carbonate and 1 part of nitre for 20—30 minutes. The fused mass is extracted with hot water, and the filtrate, after the addition of sulphuric acid, is gently heated to expel most of the nitrous fumes. The whole is now diluted to 400 c.c., 3 grams of crystallised sodium sulphite are added, and the liquid boiled until no more sulphur dioxide is evolved. It is then titrated while hot with  $N/20$  potassium permanganate until the pink colour is permanent for half a minute.

*Estimation of Vanadium in Ferro-Vanadium Steels.*—The hydrochloric acid solution is oxidised with potassium chlorate and evaporated in a platinum crucible; the residue is fused with the oxidising mixture and treated as in the former case. The theory of the process is that sulphur trioxide reduces vanadium pentoxide to the state of tetroxide, which is reoxidised by permanganate to the pentoxide. L. DE K.

**Bismuth Assay.** By A. W. WARWICK and T. D. KYLE (*Chem. News*, 1902, 85, 3—4).—One gram of finely crushed ore is evaporated

to dryness with 5 to 10 c.c. of concentrated nitric acid, the residue is warmed with 5 c.c. of nitric acid, and treated first with 25 c.c. of water, then made up to 100 c.c. with hot water. The solution is boiled vigorously for 5 minutes with 5 grams of ammonium oxalate, and the solution and subsequent washings are decanted through a filter. The precipitate is boiled with successive quantities of about 50 c.c. of water until a filtrate neutral to litmus is obtained. The basic bismuth oxalate is dissolved by warming with 2 to 5 c.c. of hydrochloric acid diluted with an equal quantity of water, the solution made up to 250 c.c. with hot water, neutralised with ammonia, and the precipitate redissolved by dilute sulphuric acid (1 of acid to 4 of water), which is added a few c.c. in excess. The solution is then titrated with permanganate.

D. A. L.

**Estimation of Hardness in Water.** By W. APPELIUS (*Chem. Centr.*, 1902, i, 137; from *Bull. assoc. belge Chimistes*, 15, 322—325).—Hehner's process of titrating water with standard hydrochloric acid, using methyl-orange as indicator, is very accurate for the temporary hardness, but is less suitable for the estimation of the permanent hardness, in which case Clark's process is preferable.

L. DE K.

**Apparatus for the Mechanical Analysis of Soils.** By A. GAWALOWSKI (*Zeit. anal. Chem.*, 1901, 40, 776—781).—Two forms of apparatus are described for the separation of the soil constituents of different degrees of fineness. The first is a conical flask through which a current of water is drawn by a syphon which can be depressed to different depths (indicated by graduations on the vessel). The second is a nest of three spherical sieves, the innermost of which has meshes 2 mm. square, the next meshes of 1 mm., and the outermost meshes of 0.5 mm. The weighed soil is placed in the inner sieve and the nest is hung in running water by a cord, and is occasionally gently shaken until the water is no longer rendered turbid. The three sieves are then dried and their contents weighed. The results obtained with both forms agree closely with those yielded by Nöbel's levigation apparatus.

M. J. S.

**[Examination of Lemon Oil.]** By HERBERT E. BURGESS and J. F. CHILD (*J. Soc. Chem. Ind.*, 1902, 21, 1176—1182).—The authors state that the determination of the specific gravity, optical rotation, and percentage of citral, coupled with the rotation after distilling the first 10 per cent. are by no means adequate to guarantee the genuineness of the samples.

According to the B. P. and other books of reference, the sp. gr. of the oil varies from 0.857—0.860, but according to the authors even 0.857 is too high a standard. The optical rotation proves that a range of  $\alpha_D + 58^\circ$  —  $+ 63^\circ$  (100 mm. tube) is quite compatible with a genuine oil; the observations may be made at a temperature of 15—20°. The fractional distillation test, namely, the determination of the rotation of the first 10 per cent., which, according to the B. P., should not differ more than 2° from the original sample, is, in the authors' opinion, absolutely worthless. For the estimation of citral, four methods have

been proposed; of these, the treatment with a saturated solution of sodium hydrogen sulphite and Tiemann's process with normal sodium sulphite are the most trustworthy, as they give almost theoretical results. The percentages of citral as found by the authors is about 4, such a percentage as 7 or 8 being highly improbable.

The usual adulterants are: lemon terpenes, turpentine, lemon grass oil, citral, and less frequently, distilled lemon oil, cedarwood oil, and stearin.

These may be detected by the determination of the sp. gr. at 15°, the optical rotation in a 100 mm. tube, the refractive index at 20°, the percentage of citral, and finally, by fractional distillation. The latter is carried out as follows: 100 c.c. of the sample are put into a distilling flask having three bulbs blown in the neck and fitted with cork and thermometer. This is connected to a condenser with a suitable receiver having two vessels graduated at 10 c.c. and 80 c.c. A Brühl's apparatus answers the purpose. The whole is exhausted and a pressure of not more than 15 mm. should be maintained. The flask is then gently heated by means of an oil-bath. The first 10 c.c. should not take less than 7 minutes to distil. The next vessel is then put into position and the distillation continued until 80 c.c. have passed over. The pressure is then relieved, and the residual oil distilled over with steam, the quantity so obtained being carefully noted. The three fractions are then examined by the polariscope, and by Zeiss's refractometer.

Tiemann's process for the estimation of the citral has been slightly modified by the authors: A saturated solution of sodium sulphite is prepared and made faintly alkaline to phenolphthalein by means of sodium hydroxide. To 50 c.c. of this solution, 25 c.c. of the oil are added, and also two drops of an alcoholic solution of phenolphthalein; the whole is then heated on a water-bath nearly to the boiling point, the vessel being constantly shaken. Sulphurous acid is added drop by drop until the red colour no longer returns. The residual oil is then measured as usual.

Tables are given showing the analytical figures of undoubtedly genuine oils, oils adulterated with terpenes, turpentine and citral, and of terpeneless oils of lemon; also the results of their fractional distillation. With the aid of these tables any gross adulteration may be readily detected.

L. DE K.

**Estimation of Ethyl Alcohol by Nicloux's Method.** By M. E. Pozzi-Escot (*Ann. Chim. anal.*, 1902, 7, 11—12).—The author has tried Nicloux's process based on the reduction of an acid solution of potassium dichromate, and states that "all the alcohols which may occur in fermented liquids behave in the same way as ethyl alcohol, and aldehyde itself exercises a reducing action notwithstanding Nicloux's denial of the fact."

L. DE K.

**Clinical Detection and Estimation of Dextrose in Urine by means of *o*-Nitrophenylpropionic Acid.** By GUGLIELMO RUINI (*Gazzetta*, 1901, 31, ii, 445—451).—According to the author's results, the best solution of *o*-nitrophenylpropionic acid for the detection of dextrose in urine is prepared by dissolving 0.3 gram of the acid in

100 grams of quite cold 6 per cent. sodium hydroxide solution; this scarcely alters when kept. The urine is boiled for a short time with the solution and immediately after cooling the liquid is mixed with chloroform, to which the indigotin formed imparts a more or less intense violet coloration. The reaction is more striking if the urine is previously clarified by means of neutral lead acetate solution, but this cannot be done if hydrogen sulphide or any other sulphide is present. The reaction is not affected by albumin, hemi-albumose, peptones, uric or hippuric acid, the pigments, or by various salts among which are the hyposulphites found in the urine of the dog. Some substances however, which are not definitely determined, but which probably include creatinine and glycuronic acid, give the indigo reaction, but only when so much as 30 drops of the urine are employed for the test; these compounds are only partially thrown down by the addition of lead acetate, but they are completely precipitated by mercury salts. In such cases, the author has found it useful to compare the reactions of the urine before and after removing the dextrose by fermentation with pure beer yeast. Bearing in mind these considerations, the indigo reaction gives a sufficiently accurate measure of the sugar in urines, especially in those slightly diabetic. The estimation is made by determining the volume of the urine (in drops) necessary to give a violet coloration to the chloroform and comparing the results obtained with urines containing known proportions of dextrose (0.2—5 grams per 100 c.c.); if much sugar is present, the urine must be suitably diluted before applying the test.

A few urines have been examined after ingestion by the patient of various drugs, but in no case has any influence on the indigo reaction been detected.

T. H. P.

**Estimation of Small Quantities of Dextrose in Urines and in Organic Liquids in General.** By ENRICO REALE (*Gazzetta*, 1901, 31, ii, 452—460).—When liquids containing small quantities of dextrose, and especially certain urines, are heated with Fehling's solution, a clear filtrate cannot be obtained by using a filter paper or an asbestos filter, owing, in some cases, to the very fine state of division of the cuprous oxide, and in others to the simultaneous precipitation of some of the copper in the form of cuprous hydroxide. In such cases, the author finds that good results are obtained with a filter prepared by placing an ash-free filter paper in a funnel and treating it first with yellow ammonium sulphide solution, and then for five minutes with dilute sulphuric acid (1 : 2); by this means, the pores of the paper are charged with a layer of finely divided sulphur, which always gives a clear filtrate after the first few drops of the liquid have passed through it. After washing, the filter and precipitate are dried in the oven, the precipitate being then removed as far as possible to a weighed platinum crucible, the filter burnt and the ash also placed in the crucible; the precipitate is then heated to redness in a current of hydrogen for a quarter of an hour, and, after cooling, weighed. The weight of cuprous sulphide thus obtained, multiplied by 0.7987, gives the corresponding quantity of copper, from which the amount of dextrose is given by means of Allihn's tables. It is found

that the warm Fehling's solution has a negligible action on the sulphur and the small quantity of ammonium sulphide held by the filter paper. A series of comparative estimations of the dextrose in urines, using sulphur filters and ordinary asbestos filters, shows that the former, although they act rather more slowly than the latter, give almost theoretical results, whilst when asbestos is employed, very low values are obtained.

T. H. P.

**Reaction for Mannitol.** By HENDRIK WEFERS BETTINK (*Ned. Tijdschr. Pharm.*, 1901, 13, 321–322).—0.01 gram of the substance is dissolved in 1 c.c. of dilute sulphuric acid, 3 drops of a solution of potassium dichromate (1 : 25) are added, and the mixture boiled for 1 minute. The solution is then made slightly alkaline with sodium hydroxide, filtered, and boiled with 1 c.c. of Fehling's solution. On oxidation, mannitol is converted into the corresponding aldehyde, *d*-mannose, which has a strong cupric reducing power.

It is, of course, necessary first to ascertain whether the mannitol contains any added reducing substances or sucrose; the presence of the latter may be detected by the gradual formation of a brown coloration when 0.05 gram of the substance is dissolved in 3 c.c. of sulphuric acid to which 1 drop of water is then added; pure mannitol remains practically unchanged for a few hours.

L. DE K.

**Estimation of Volatile Acids in Wine.** By J. DUGAST (*Ann. Chim. anal.*, 1902, 7, 19).—A reply to Curtel (this vol., ii, 55). The author states that the estimation of the volatile acidity by taking the difference between the total and fixed acidity is not more correct than the direct estimation of the acidity in the distillate.

The fixed acids, acting on the acetates, expel acetic acid, but the result is not consequently too low; exact compensation takes place. The slight error due to the presence of ethyl acetate may in most cases be overlooked. In practice, both methods give identical results.

L. DE K.

**Distinction between Ferric Citrate and Ferric Potassium Tartrate.** By PAOLO FIORA (*Chem. Centr.*, 1901, 11, 1322; from *Boll. Chim. Farm.*, 40, 696).—A few drops of a solution of silver nitrate (1 : 10) are added to a few c.c. of a highly diluted solution of the salt to be tested. If a precipitate is at once formed which disappears on shaking, the solution contains ferric citrate, whilst in the case of the tartrate the precipitate gradually increases. In the dark, the citrate solution remains unchanged, but the tartrate solution gradually blackens owing to reduced metallic silver.

L. DE K.

**Two New Methods for the Estimation of Berberine.** By HARRY M. GORDIN (*Arch. Pharm.*, 1901, 239, 638–645).—From a solution of berberine or any of its salts in absolute alcohol, the alkaloid can be precipitated by alcoholic sulphuric acid as the sulphate  $C_{20}H_{17}O_4N_4H_2SO_4$ ; the mixture should be diluted with an equal volume of ether, allowed to remain overnight, and the precipitate filtered and washed with a mixture of equal volumes of alcohol and



ether, the total volume of the filtrate and washings being noted. The precipitate is rinsed into a 200 c.c. graduated flask, 20 c.c. of 20 per cent. potassium iodide solution added, and then water to the mark, and the whole well shaken; berberine hydriodide,  $C_{20}H_{17}O_4N, HI$ , is precipitated, one equivalent of free acid remaining in solution for each molecule of berberine present. The liquid is filtered, and 100 c.c. of the filtrate are titrated with  $N/40$  potassium hydroxide, phenolphthalein being used as the indicator. The alkali should be standardised against  $N/40$  sulphuric acid under similar conditions, the alkaloid being omitted, of course; 1 c.c. of  $N/40$  alkali, used in titrating half of the solution = 0.01675 gram of berberine in the quantity taken, and 0.0000526 must be added for each c.c. of mother liquor and washing liquid used, on account of the solubility of berberine sulphate in a mixture of alcohol and ether.

If it is not a solution in absolute alcohol which has to be dealt with, the berberine should be precipitated with excess of 10 per cent. potassium iodide solution, the precipitated hydriodide washed with 2 per cent. potassium iodide solution and rinsed with a little water into a flask, heated at 60—70°, acetone added in volume equal to one-third of that of the water, the flask corked loosely and shaken for 10 minutes, 5 c.c. of 10 per cent. sodium hydroxide solution added, the shaking continued for 10 minutes or so until the yellow hydriodide has disappeared, or the flask warmed at 50—60° if necessary to that end, water added to the cooled contents until the acetone present amounts to one-ninth of the whole in volume, the flask allowed to remain overnight, the acetone-berberine filtered off, dried first under diminished pressure and then at 105°, and weighed. One gram of acetone-berberine = 0.853 berberine; and 0.0000273 must be added for each c.c. of the dilute acetone mother liquor, to allow for the solubility of the acetone-berberine therein. C. F. B.

**Estimation of Pepsin in Gastric Juice.** By LÉON MEUNIER (*J. Pharm. Chim.*, 1901, [vi], 14, 555—557. Compare Abstr., 1901, ii, 342).—One gram of casein and 0.5 c.c. of pure hydrochloric acid are added to 14 c.c. of the gastric juice and the whole vigorously shaken. After the casein has settled to the bottom of the vessel, the amount of free hydrochloric acid is estimated in a portion of the clear liquid. The remainder is then heated at 40° for 24 hours and the free hydrochloric acid again estimated. The difference between these two numbers gives the pepsin value of the gastric juice. H. R. LE S.

**Testing Albuminous Urines.** By L. PORTES and A. DESMOULIÈRES (*Ann. Chim. anal.*, 1901, 6, 442—443).—A useful tabular scheme for testing urines for nucleoalbumins, mucin, globulin, albumins soluble in acetic acid, serin, albumoses, and peptones according to recognised methods. L. DE K

## General and Physical Chemistry.

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**Some Phenomena connected with the Combination of Hydrogen and Chlorine under the Influence of Light.** By P. V. BEVAN (*Proc. Camb. Phil. Soc.*, 1902, 11, 264—266).—Using an apparatus essentially the same as that of Bunsen and Roscoe, the author has studied the connection between the initial expansion, the accompanying rise of temperature, and the amount of hydrogen chloride formed when a mixture of hydrogen and chlorine is exposed to light. It is shown that the initial expansion occurs only when the hydrogen and chlorine combine and is due to the heat liberated by the combination. The author's results differ from Pringsheim's (*Ann. Phys. Chem.*, 1887, 32, [iii], 384). J. C. P.

**Quantitative Spectra of Beryllium.** By W. NOEL HARTLEY (*Proc. Roy. Soc.*, 1902, 69, 283—285).—Solutions of beryllium salts of diminishing concentration have been spectroscopically examined and the gradual extinction of the characteristic lines has been noted. Two lines,  $\lambda$  3130.3 and 2478.1, are still visible when the concentration of the beryllium has fallen as low as 0.000001 per cent. J. C. P.

**Dispersion of the Magnetic Rotation of the Plane of Polarisation in Negatively Rotating Salt Solutions. II. Further Measurements with Potassium Ferricyanide.** By L. H. SIERTSEMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 4, 339—341).—For potassium ferricyanide there appears to be no distinct variation of the rotation constant with the concentration. J. C. P.

**Attempt at a Theory of Phosphorescence of Long Duration, especially of the Sulphides of the Alkaline Earths.** By L. E. O. DE VISSER (*Rec. Trav. Chim.*, 1901, 20, 435—456).—Pure barium sulphide, prepared from barium carbonate and sulphur, does not phosphoresce; traces of bismuth induce phosphorescence, a maximum being reached when the proportion of bismuth to barium is as 2 atoms to 100,000 atoms. Similarly, the phosphorescence of calcium sulphide decreases with the purity of the substance.

At the ordinary temperature, phosphorescence is recognisable one month after the exposure to light; at a low temperature, the phosphorescence is less obvious, but remains for a longer period, whilst at a higher temperature the reverse is the case. The author discusses the interpretation of these phenomena. K. J. P. O.

**Chemical Action of the Cathode Rays.** By GERHARD C. SCHMIDT (*Ann. Physik*, 1902, [iv], 7, 321—332).—When ferric and mercuric chlorides are exposed to the action of the cathode rays, reduction takes place in both cases, as can be shown by testing with ferricyanide and ammonia respectively; in like manner, silver and mercurous chlorides darken on exposure to the cathode rays, owing in

the first case to the formation of a subchloride. The colour changes shown by sodium and potassium chlorides when subjected to the action of the cathode discharge are attributed to the formation of subchloride, and the grounds for this conclusion (see Wiedemann and Schmidt, *Abstr.*, 1898, ii, 291) have been confirmed. In interpreting the action of the cathode rays in the above cases, the author considers that the negatively charged electrons satisfy the positive valency of the metal, which is then no longer able to retain the whole of the acid radicle; the latter, if volatile, escapes. In cases, such as mercuric, barium, and strontium sulphates, where the acid radicle is not volatile, the cathode rays probably cause a dissociation into ions, and only eventually a slight reduction.

J. C. P.

**Some Properties of the Radiations from Radio-active Substances.** By HENRI BECQUEREL (*Compt. rend.*, 1902, 134, 208—211).—It has been previously shown that the radiations emitted by radium partly consist of those which are deflected in a magnetic field, partly of radiations not deflected, which are further divisible into those easily absorbed and those very penetrative. The radiations emitted by uranium had been previously shown to contain deviable rays (*Abstr.* 1900, ii, 518); further work has failed to detect any of the other, that is, the non-deviable rays, but it does not prove the entire absence of at least the penetrative rays, the action of which on a photographic plate is exceedingly slow. The radiations are also found to chiefly consist of those of radium which are least deviated. The rays which are deflected are shown to be those which are most active in effecting the transformation of white phosphorus into red, whilst the penetrative non-deviated rays have no appreciable action. It is probable that those rays, non-deviated but easily absorbed, would also be active in this respect, but the conditions of the experiment precluded their activity being rendered evident (this vol., ii, 57).

L. M. J.

**Theory of Oxidation and Reduction Elements.** By CARL FREDENHAGEN (*Zeit. anorg. Chem.*, 1902, 29, 396—458).—Assuming with Ostwald that oxidation consists in increasing the positive or diminishing the negative charge, then all cells may be classed together as oxidation elements. The chemical activity of the cells may be due to actions of the three types: (1)  $\text{Cu} + \oplus = \text{Cu}^+$ , (2)  $\text{Fe} + \oplus = \text{Fe}^{++}$ , and (3) formation of new ions from a complex ion. The author has studied cells belonging to the second type. Peters' results (*Abstr.*, 1898, ii, 419) on the potential in a solution containing ferrous and ferric ions have been confirmed, and the formula which he developed is found to be correct. Experiments made with cuprous and cupric, stannous and stannic, manganate and permanganate, and sulphate and persulphate solutions also prove the validity of Peters' formula.

Platinum electrodes in some oxidising solutions show a constant potential immediately after immersion, whilst in others it is variable, and this indicates that the velocity of reaction of the ions of the oxidising solution with the gases absorbed by the platinum is very variable. It has been established that in oxidation elements the

platinum electrodes always become charged with gases; in some cases, the potential measured is entirely due to this gas charge, and is in no way conditioned by the giving up of electron from the ion of the solution to the electrode. The magnitude of the gas charge is dependent on the hydrogen ion concentration in the liquid, but the potential of the oxidising agent is absolutely independent of this.

Potential difference measurements with mixed acid or alkaline solutions of potassium ferrocyanide and ferricyanide give results which show deviations from Peters' formula.

The conditions for the existence of ions in aqueous solution are discussed, and it is shown that when the electrolytic potential is smaller than  $-1.08$ , the higher stage of oxidation of a substance is only stable when the concentration is less than normal in normal acid solution. When the electrolytic potential is greater than 0, the lower stage of oxidation of an ion is not stable in normal concentration in normal acid solution.

In an electromotive respect, an ion is inactive when neither a higher nor a lower stage of oxidation of it is capable of existing in the solution in appreciable quantity.

Using platinum electrodes, the potential measured in hydrogen peroxide solutions is not due to the oxidising action of the substance but to secondary causes. Hydrogen peroxide is to be regarded in this respect as a peracid; its oxidising power is due to the change of  $(\bar{O}-\bar{O})$  into  $2\bar{O}$ , its reducing power to the change of  $(\bar{O}-\bar{O})$  into  $O_2$ .  
J. McC.

**The Nitrogen-Hydrogen Gas Element.** By E. BAUR (*Zeit. anorg. Chem.*, 1902, 29, 305—325).—The *E.M.F.* of the element has been determined, the gases being contained over ammonia which contains  $N'''$  and  $H^+$  ions. Liquid ammonia was found to be inconvenient, and the liquids used were Divers' fluid (ammonium nitrate saturated with ammonia) and saturated aqueous ammonia. The most constant results were obtained when the former electrolyte was employed. The *E.M.F.* is 0.590 volt at  $-10^\circ$ . The *E.M.F.* sinks rapidly when current is drawn from the cell, but regains its normal value on standing, and this indicates that the current is produced by the union of nitrogen and hydrogen to form ammonia.

The decomposition tension of the two electrolytes has been determined by the methods of Glaser (*Abstr.*, 1899, ii, 78) and Bose (*Abstr.*, 1899, ii, 348). There is an evident break in the curves obtained, but on account of the small concentration of the ions in the liquid, the point is not particularly sharp.

Unsuccessful attempts were made to combine nitrogen and hydrogen directly over platinum black and over chromium nitride; no ammonia was produced.  
J. McC.

**Variation of Electromotive Force and of the Temperature Coefficient of the Daniell Cell with the Concentration of the Sulphate of Zinc.** By J. CHAUDIER (*Compt. rend.*, 1902, 34, 277—279).—The *E.M.F.* of a Daniell cell was determined when the concentration of the zinc sulphate varied from 0 to 200 per 100 of water, and the temperature

coefficient was found at each concentration, the solution of copper sulphate being saturated throughout. It was ascertained that with increasing concentration of the zinc sulphate, the *E.M.F.* at first increases, reaching a maximum of 1.1368 when the concentration of the zinc sulphate is 0.5 after which it decreases, being 1.0902 for the saturated solution. The temperature coefficient is negative for the low concentrations, becomes positive at about 0.5 per cent., and again negative at from 7 to 8 per cent. When the concentration of the zinc sulphate is either of these values, the *E.M.F.* of the Daniell cell is independent of temperature. It also follows that the variation of the heat of the reaction with dilution varies in a corresponding way.

L. M. J.

**Current and Energy Efficiencies obtainable in the Electrolytic Preparation of Alkali Hypochlorites and Chlorates.** By FRITZ FOERSTER and ERICH MÜLLER (*Zeit. Elektrochem.*, 1902, 8, 8—17).—By the use of a platinum anode coated with platinum black, and by the addition of a chromate to the alkali chloride solution, the current efficiency in the electrolytic preparation of alkali hypochlorites may be made almost equal to the theoretical value. By employing a small current density, the *E.M.F.* required may also be made to approach very closely to the theoretical 2.2 volts. For example, the authors obtained a 96 per cent. current efficiency using an *E.M.F.* of 2.4 volts.

The current efficiency in the preparation of chlorates may be raised to nearly 95 per cent., by adding to the electrolyte quantities of hydrochloric acid sufficient to maintain the ratio of hypochlorous acid to hypochlorite between the limits 2:1 and 1:2. The presence of a chromate is necessary in this case also. These results confirm Foerster's theory of the formation of chlorate (*Abstr.*, 1899, ii, 278, and 1900, ii, 72).

T. E.

**Electro-affinity as a Basis for the Systematisation of Inorganic Compounds.** By JAMES LOCKE (*Amer. Chem. J.*, 1902, 27, 105—117).—The author discusses Abegg and Bodländer's theory (*Abstr.*, 1899, ii, 542) in its connection with the solubility of salts, formation of complexes, and stability on ignition. It is shown that the behaviour of thallium salts is not in conformity with what is to be expected, according to the theory, from the decomposition voltage of thallium. The general behaviour of cuprous, barium, zinc, and caesium salts does not agree with the predictions of the theory, and the solubility relationships of many alums (*Abstr.*, 1901, ii, 656) are directly opposed to it. The author thinks that little useful purpose is served by Abegg and Bodländer's speculations.

J. McC.

**Spontaneous Ionisation of Gases.** By C. T. R. WILSON (*Proc. Roy. Soc.*, 1902, 69, 277—282).—This continuation of previous work (*Abstr.*, 1901, ii, 435) deals with the ionisation of air, hydrogen, carbon dioxide, sulphur dioxide, and chloroform vapour. As before, the rate of leak from a charged conductor is found to be proportional to the pressure, except for high values of the latter. The rates of

production of ions in air, carbon dioxide, sulphur dioxide, and chloroform vapour (hydrogen is an exception) are very nearly in the ratio of the densities of the gases. In noting the similarity of these results to those obtained by Strutt (*Phil. Trans.*, 1899, 196, A, 507), when the above gases were exposed to the action of radium and polonium rays, the author suggests that the ionisation may be due to radiation from the walls of the vessel.

J. C. P.

**Measure of the Electrolytic Diffusion, Transport Numbers, and Mobility of the Ions.** I. By PAOLO STRANEO (*Atti R. Accad. Lincei*, 1902, [v], 11, i, 58—65).—The author brings forward a method for measuring the coefficient of diffusion,  $D$ , the transport number  $n$ , and the relative mobilities,  $u$  and  $v$ , of the ions of an electrolyte, which obviates the use of diaphragms and requires only very small differences of concentration, besides being very rapidly carried out.

The principle of the method is to place the electrolyte to be examined between two horizontal electrodes at a short distance apart, and by means of an electric current of convenient density to cause a displacement of the electrolyte from the top to the bottom; from the variations of the concentration of the electrolyte in the neighbourhood of the electrodes, the values of  $D$ ,  $n$ ,  $u$ , and  $v$  can be calculated. A description of the apparatus is given, and also the mathematical reasoning required for the calculations. A test experiment with zinc sulphate solution between amalgamated zinc electrodes gave good results.

T. H. P.

**Measurement of Ionic Velocities in Aqueous Solution, and the Existence of Complex Ions.** By BERTRAM D. STEELE (*Phil. Trans.*, 1901, 198, A, 105—145).—Details are given of work previously published (*Trans.*, 1901, 79, 414), and the results of further experiments are recorded. The following new indicators have been used; as cation indicators, magnesium chloride with magnesium oxide suspended in the solution, potassium chloride containing dissolved potassium carbonate, silver nitrate with silver anode, aluminium sulphate with aluminium hydroxide suspended in the solution; as anion indicator, potassium fluoride, containing a small quantity of acetic acid. The new transport numbers recorded in this paper are chiefly those of salts like barium chloride and magnesium sulphate. It is found that in these cases, which deviate from the simplest type, (1) the transport number is not independent of the concentration; (2) the specific ionic velocity of the cation varies with the particular salt studied; (3) the current as measured by the galvanometer is not the same as that calculated from the observed velocity of the margin. The explanation that the specific ionic velocity varies with the concentration, and varies more for some ions than for others, does not commend itself to the author, and he prefers to attribute the exceptional behaviour of such salts to the formation of complex ions in solution (compare Noyes, *Abstr.*, 1901, ii, 143). This means a motion of at least a portion of the undissociated salt along with the ions, and consequently the concentration of the solution within the margin may be

altered; this interferes with the regularity of the potential fall, and the velocity of the margin is correspondingly affected. Experimental evidence of such changes of concentration within the margin is recorded in the paper.

J. C. P.

**Melting of Dissociating Compounds.** By FRANK AUSTIN LIDBURY (*Zeit. physikal. Chem.*, 1902, 39, 453—467).—It has been shown by Roozeboom that many hydrates may at the same temperature be in equilibrium with solutions containing respectively more or less water than the hydrate itself (Abstr., 1893, ii, 119). According to the expression deduced by Roozeboom, the temperature-concentration curve of the solution in equilibrium with the hydrate should be perfectly continuous with a maximum corresponding with the melting point of the hydrate. This result, however, was not confirmed by his own experiments in the case of the hexahydrate of calcium chloride, or by the determinations of Le Chatelier. The author has therefore carefully redetermined the temperature-concentration curve of solutions in equilibrium with  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  for solutions of composition varying from  $\text{CaCl}_2 \cdot 5.54\text{H}_2\text{O}$  to  $\text{CaCl}_2 \cdot 6.44\text{H}_2\text{O}$ . He finds the curve is perfectly continuous with a maximum at  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . Similar results were also obtained for the equilibrium of the solid compound of aniline and phenol with the liquid mixture, the results, however, not possessing so high a degree of accuracy. The variation of crystallisation velocity for  $10^\circ$  of undercooling was also determined in the calcium chloride system, and it was found to increase continually with addition of water. In the case of sulphuric acid, however, the addition of small quantities of either sulphur trioxide or water greatly lowers the crystallisation velocity, this behaviour being typical of a compound which does not dissociate, or does so to but a slight extent, during melting.

L. M. J.

**Experimental Researches on the Measurement of Critical Constants.** By PHILIPPE A. GUYE and ED. MALLET (*Arch. Sci. phys. nat.*, 1902, 13, 30—40; 129—143).—The papers form the first two of a series, the first is largely historical and deals with the views of various authors on the state of matter under the critical conditions. The authors consider it established that the two states become identical at the critical temperature, above which only one fluid form exists. The disappearance of the meniscus and formation of the cloud determine the critical temperature, and many of the differences found by previous observers between the two phenomena are due to inequalities of temperature, whilst impurities and also partial decomposition before the critical temperature account for many divergencies. The authors enforce the necessity of having the liquid enclosed in a tube the capacity of which is equal to the volume at the critical point of the quantity employed. In the second paper, the authors give an account of the method and apparatus employed in their determinations. For the determination of the critical temperature and pressure, the methods employed by Altschul were used (*Zeit. physikal. Chem.*, 1893, 11, 577) and various sets of experiments are given in order to show the trustworthiness of the apparatus. As tests of the purity of the compounds, the indices

of refraction and the viscosity coefficients were determined. The results are postponed to later communications. L. M. J.

**Critical Constants and Molecular Complexity of some Organic Compounds.** By PHILIPPE A. GUYE and ED. MALLET (*Compt. rend.*, 1902, **34**, 168—171).—The following results have been obtained in continuation of those previously recorded (this vol., ii, 195). The tables contain the values of the critical constants and of the ratios which serve as the criteria of complexity (*loc. cit.*):

Compound.	$T_c$ .	$P_c$ .	$K_c$ .	$MR/K_c$ .	$D_c/D$ .	$f$ .
Anisole .....	641·5	41·25	15·55	2·03	3·91	3·19
Phenetole .....	647·0	33·8	19·14	1·89	4·14	3·32
<i>m</i> -Cresol .....	705·0	45·0	15·67	2·01	4·11	3·40
Aniline .....	698·8	52·4	13·34	2·17	4·00	3·22
Dimethylaniline .....	687·7	35·6	19·32	2·00	4·16	3·26
Dimethyl- <i>o</i> -toluidine .....	667·8	30·8	21·68	1·97	4·08	3·24

None of these compounds therefore show appreciable polymerisation above the boiling point.

Acetonitrile .....	543·2	47·7	11·39	0·95	5·93	3·15
Propionitrile .....	558·7	41·3	13·53	1·14	5·22	3·16
Butyronitrile .....	582·1	37·4	15·56	1·28	4·86	3·17
Hexonitrile .....	621·8	32·1	19·34	1·50	4·46	3·37
Benzonitrile .....	699·2	41·6	16·81	1·79	4·48	3·16

The nitriles are polymerised at the critical state, the polymerisation decreasing as the series is ascended. It is very marked for acetonitrile, being greater than for acetic acid. L. M. J.

**Vapour Pressure in the System, Water-Acetone-Phenol. I.** By FRANZ A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1902, **39**, 485—510; see Abstr., 1900, ii, 393).—The vapour pressure and composition of the vapour were first determined for the system water—phenol at temperatures between 29·8° and 64·4°. In each case, the concentration of the phenol in the vapour phase is less than that in either of the liquid phases, so that by evaporation at any temperature the more aqueous liquid phase would finally disappear. In the system water—acetone, two liquid phases are not obtained and the vapour pressure was determined for solutions containing 8·04, 15·6, and 82·9 per cent. of acetone, whilst tables are also given for the vapour pressure of mixtures of various concentrations at 50°, 56·5°, 68°, and 75°. A diagram showing the form of the binodal curve in the ternary system is given, and the composition determined for a number of conjugate solutions. It is seen that the concentration of phenol in the more aqueous phase is lowered by the substitution of acetone for water, whilst in the other phase the concentration of phenol is at first in



creased and afterwards lowered. The critical temperature in the ternary system is  $92^{\circ}$ , above which but one liquid phase is obtainable. A large number of determinations of the vapour pressure in the ternary system were made and tables are given. Diagrams show how the pressure decreases in various acetone—water mixtures when phenol is added. It is noteworthy that of equally concentrated solutions of phenol in water and acetone, the vapour pressure of the aqueous solution is the smaller if the concentration of phenol is below 73 per cent. and *vice versa*.

L. M. J.

**Researches on Boyle's Law at Low Pressures.** By ANGELO BATTELLI (*Ann. Chim. Phys.*, 1902, [vii], 25, 308—365).—A detailed account of experiments made on the compressibility of hydrogen, oxygen, and carbon dioxide under low pressures, the results of which are summarised in the following conclusions.

Hydrogen obeys Boyle's law under pressures varying from 760 to 0.02 mm. Oxygen deviates from the law under 0.7 mm. pressure, becoming more compressible; this effect may be due to the diminution in the number of reacting molecules owing to the formation of molecular groups. A slight deviation is also noticed in the case of air between the limits of 2 mm. and 5 mm. pressure.

The compressibility of carbon dioxide under low pressures is greater than its value calculated from the law, but this is probably due to the absorption of the gas by the walls of the containing vessels, the deviation from theory being greater in glass than in iron cylinders. If these variations in compressibility are due to cohesion, then the equation  $[p + \phi(a.v.T)](\nu - b) = k$  where  $\phi(a.v.T)$  is a function which becomes discontinuous for one or more values of  $\nu$ . This communication also contains a detailed criticism of the results of earlier investigators.

G. T. M.

**True Density of Chemical Compounds and its Relation to Composition and Constitution. V. Nitrogen Compounds.** By INNOCENTIVS I. KANONNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 743—790. Compare Abstr., 1900, ii, 134, and 1901, ii, 305).—The author has determined the true densities of nearly 300 nitrogen compounds, and from his results draws the following conclusions: (1) The molecular density of nitrogen in the free state is 89.0, but it only has this value in comparatively few of its compounds, namely, nitric acid, methyl nitrate, ethylene nitrate, glyceryl nitrate, the oxalazines, nitric oxide, and nitrogen peroxide. In its other compounds, nitrogen possesses molecular densities depending on, and varying with, its valency. Thus, for trivalent nitrogen, the molecular density has the value 56.6; for quinquivalent, 45.0; and for septavalent, 33.4. Change of valency of a nitrogen atom in a compound is usually accompanied by a disappearance of double bonds between carbon atoms. (2) Nitrogen entering a closed ring of carbon atoms exerts no influence on the increase produced by such a ring on the molecular density of the compound, namely, 8.7. (3) Double, and, in general, more complex, linkings between nitrogen atoms and between nitrogen and carbon have

no influence on the magnitude of the molecular density. (4) A double linking between an atom of nitrogen and one of oxygen influences the molecular density to the same extent as a double linking between carbon and oxygen, which causes an increase of 4.84. (5) The grouping  $\begin{smallmatrix} \text{N} \\ \text{C} \end{smallmatrix} > \text{O}$  or  $\begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} > \text{O}$ , produces the same change in the molecular density of a compound containing it as does the grouping  $\begin{smallmatrix} \text{C} \\ \text{C} \end{smallmatrix} > \text{O}$ , that is, the value is diminished by 7.74.

T. H. P.

**Molecular Surface Energy of Solutions. Molecular Weight of Sulphur.** By DESIDERIUS PEKÁR (*Zeit. physikal. Chem.*, 1902, 39, 433—452).—The method for the determination of the surface tensions is described; it consists essentially in the comparison of the curvature of the liquid contained in a narrow vessel with that of a liquid of known surface tension. The molecular surface energy was determined in the case of ethyl ether, carbon disulphide, and benzene. The values of the critical temperatures [that is, the temperatures at which  $\gamma(Mv)^{\frac{1}{3}} = 0$ ] for the compounds were found to be respectively, 187.7°, 271.0°, and 274°, whilst the mean temperature coefficients are 0.230, 0.203, 0.233, indicating non-associated liquids (these numbers are not expressed in the same units, and are not directly comparable with those of Ramsay and Shields). In the case of mixtures of these compounds, although the molecular surface energy itself may not be the additive mean, yet the temperature coefficient is still normal, and hence, if the molecular weight of one component of a mixture is known, that of the other is calculable. This result is in accord with that of Ramsay and Aston (*Abstr.*, 1895, ii, 40), with which work, however, the author was not familiar until the end of his research. The molecular weight of sulphur was then ascertained by means of the determination of the molecular surface energy of its solution in carbon disulphide and in disulphur dichloride. In both solvents, it was found that the dissolved sulphur has a molecular weight corresponding with  $S_6$  or  $S_8$ , a result in accord with most determinations, but not with those of Orndorff and Terrasse, who, by the cryoscopic method, obtained the value 61.9 for the molecular weight of sulphur in disulphur dichloride solution (*Abstr.*, 1896, ii, 358).

L. M. J.

**Liquid Sulphur Dioxide as a Solvent.** By PAUL WALDEN and M. CENTNERSZWER (*Zeit. physikal. Chem.*, 1902, 39, 513—596. Compare *Abstr.*, 1900, ii, 10).—The conductivity of pure liquid sulphur dioxide at 0° is  $0.9 \times 10^{-7}$  (recip. Siemens' units). This is somewhat greater than the conductivity of water and less than that of liquid ammonia. It is probable that the conductivity is due to a slight dissociation into  $SO''$  and  $O''$ , and further into  $S''''$  and  $2O''$ . The existence of the ion  $S''''$  is suggested by the proved formation of  $Te''''$  in fused tellurium tetrachloride (Hampe), which is a good conductor. The conductivity of solutions of the following salts in liquid sulphur dioxide have been determined at dilutions from  $v=8$  to  $v=2048$ ; potassium iodide, bromide, and thiocyanate, sodium iodide, ammonium iodide, and thiocyanate, rubidium iodide, methylammonium chloride, dimethylammon-

ium chloride, trimethylammonium chloride, tetramethylammonium chloride, bromide, and iodide, ethylammonium chloride, diethylammonium chloride, triethylammonium chloride, tetraethylammonium chloride, benzylammonium chloride, and trimethylsulphonium iodide. The molecular conductivities of the univalent haloids in sulphur dioxide vary from 3 to 157 at 25°. Some of the salts have a considerably higher conductivity in sulphur dioxide than in water at the same concentration. Kohlrausch's law of the independent migration of the ions seems to apply, but an additive scheme could not be satisfactorily constructed, because in most cases the maximum conductivity had not been reached when  $v = 2048$ . The results obtained are not in conformity with Ostwald's dilution law, and only for some of the salts are the modified formulæ of Rudolphi and van't Hoff valid. Of the inorganic iodides, the rubidium salt is the best conductor, then follow potassium, ammonium, and sodium. Tertiary substituted ammonium salts are better conductors than secondary, and these again conduct better than primary; there is a large change on passing from a tertiary to a quaternary ammonium salt. Salts with isomeric cations have not the same conductivity.

Iodine, mercuric iodide, and cadmium iodide dissolve more readily in solutions of potassium iodide and rubidium iodide than in the pure solvent, and this proves that formation of complexes takes place. The solutions of the complex compounds conduct better than those of the substance from which they are produced.

The conductivities of the solutions have been determined at temperatures from about  $-67^{\circ}$  upwards. The conductivity at first increases to a maximum and then falls. When certain solutions are heated, separation of solid or decomposition takes place, but others can be heated up to and even beyond the critical point and an apparently homogeneous solution remains. The conductivities of the latter have been determined up to the critical point (hydrochloric acid, quinoline, triamylammonium iodide, benzylammonium chloride, and trimethylsulphonium iodide). The conductivity continuously decreases as the temperature rises, and in all cases disappears at the critical point. The authors conclude from this that electrolytic dissociation is associated with the liquid condition; they show that there is a parallelism between dissociating power and surface tension of a number of solvents (both of these become zero at the critical point); and they discuss the connection between dissociating power and dielectric constant, medial energy, latent heat of vaporisation, and the association factor of the solvent.

Using the Walker and Lumsden modification of the Landsberger method, the rise in boiling point of the sulphur dioxide due to dissolved substance has been determined. The latent heat of vaporisation of sulphur dioxide, obtained from the vapour tension curve, is 92.45, and by direct experiment 91.7 and 91.2 have been found. Using the mean value, the molecular rise of boiling point 15.0 is obtained by van't Hoff's formula. Non-electrolytes (toluene, acetanilide, naphthalene, diisobutyl tartrate, and  $\beta$ -naphthol picrate), gave normal values for the molecular weight. The values obtained for electrolytes are, with out exception, abnormal, but not similar to those found in aqueous

solution. The values being too low, the authors are forced to assume that the electrolytes are associated as well as dissociated in sulphur dioxide solution. The salts can be divided into two groups, one in which the value of  $i$  is greater than 1 (up to 1.3), and another where the value of  $i$  is less than 1. As the dilution increases, the value of  $i$  diminishes in the former case and increases in the latter, so as to converge towards 1 in all cases at high dilution. On account of the degree of polymerisation being unknown, it is not possible to calculate the degree of dissociation from the  $i$  values; the degree of dissociation as calculated from the conductivity is also complicated by the association. The authors think it probable that association takes place both between dissolved molecules themselves, and between these and solvent molecules.

J. McC.

**Absorption of Gas in Organic Solvents and in their Solutions.** By G. LEVI (*Gazzetta*, 1901, 31, ii, 513—541).—The author's determinations of the solubility of gases were carried out by means of a somewhat modified form of the apparatus described in Ostwald's *Lehrbuch allegem. Chem.*, 2nd Ed., 1, 615. From measurements of the solubilities of oxygen, methane, and ethylene at various temperatures in methyl alcohol and acetone, the following conclusions are drawn: (1) Methyl alcohol and acetone have almost equal solvent powers for gases. (2) With increase of temperature, the solubility decreases regularly according to the general law of gaseous absorption.

Further, determinations of the solubility of nitrogen in methyl alcohol and in methyl alcoholic solutions of potassium iodide and carbamide at various temperature lead to the following deductions: (1) Jahn's empirical law,  $(\alpha - \alpha_1)/M^{\frac{1}{3}} = \text{a constant}$ , found to hold exactly for aqueous solutions of electrolytes, and less so for aqueous non-electrolytes, holds also for the solutions employed by the author; the law must here be expressed by  $(l - l_1)/M^{\frac{1}{3}} = \text{a constant}$  where  $l$  and  $l_1$  are the solubilities of the gas in the pure solvent and in the solution at the same temperature and  $M$  is the number of gram-mols. of the substance in unit volume of the solution. The law  $C_1/C_2 = 1$ , arrived at theoretically by Jahn, holds, in the case of methyl alcoholic solutions, very well for solutions of non-electrolytes and not quite so well for those of electrolytes;  $C_1$  and  $C_2$  here represent the molecular concentrations of the gas in the solvent and the solution respectively.

T. H. P.

**Inorganic Solvent and Ionising Media.** By PAUL WALDEN (*Zeit. anorg. Chem.*, 1902, 29, 371—395. Compare Abstr., 1901, ii, 11).—Arsenic tribromide (melting point  $31^\circ$ ) is a solvent for many salts; its conductivity at  $33^\circ$  is  $\lambda = 1.53 \times 10^{-6}$ . Solutions of antimony triiodide, stannic iodide, ferric chloride, and tetraethylammonium iodide in arsenic tribromide possess only a comparatively small conductivity but sufficient to indicate that ionisation takes place. The value for the molecular depression of the freezing point is 189. Abnormal results have been obtained for the depression of the freezing point with electrolytes, and as these cannot be due to ionisation, it is probable that interaction takes place between the solvent and the

dissolved substance; the abnormality may, however be due to isomorphism of solvent and dissolved substance.

Chlorosulphonic acid ( $\lambda = 0.16 \times 10^{-3}$  at  $25^\circ$ ) has a small ionising power, whilst sulphuric acid ( $\lambda$  about the same as that of  $1/10N$  potassium chloride) and methyl sulphate ( $\lambda = 2.9 \times 10^{-6}$ ) also dissolve salts (both binary and ternary) and the solutions have a comparatively high conductivity.

Comparing the results obtained with those previously found (*loc. cit.*; and this vol., ii, 245) the author concludes that the group  $\text{SO}_2$  (or  $\text{SO}$ ;) has ionising properties and that these are increased by the introduction of hydroxyl groups.

A table is given of various physical properties of inorganic ionising and non-ionising solvents and it is seen that none of the theories so far proposed to account for ionising power can be considered satisfactory.

J. McC.

**Neutral Affinities.** By LEOPOLD SPIEGEL (*Zeit. anorg. Chem.*, 1902, 29, 365—370).—The author conceives that a positive and a negative electron may unite in pairs with a radicle, element, or molecule, and these, balancing each other, are inactive but otherwise the same as the electron associated with the ionic condition. When ammonia,  $\oplus\text{NH}_3$ , reacts with a positively charged ion and thus gives up its negative electron, the radicle produced has a positive charge and is basic.

The assumption of the existence of these neutral affinities which can be made active by addition to the molecule gives a new signification to Werner's coordination number, and with its aid it may be possible to connect together and explain the nature of double salts, ammonia compounds, oxonium salts, and hydrates.

J. McC.

**Velocity of Solution.** By KARL DRUCKER (*Zeit. anorg. Chem.*, 1902, 29, 459—463. Compare Abstr., 1901, ii, 376).—In reply to Bruner and Tolloczko (this vol., ii, 62; compare also Abstr., 1901, ii, 10), the author points out that the constancy of the value previously obtained by him indicates that no error has been introduced on account of small particles being rubbed off the plate and remaining in suspension in the liquid. The opinion is maintained that the constant in the Noyes and Whitney formula cannot be regarded as a diffusion coefficient.

J. McC.

**Behaviour of Molecular Compounds on Dissolution. II.** By GUIDO BODLÄNDER and R. FITTIG (*Zeit. physikal. Chem.*, 1902, 39, 597—612. Compare Abstr., 1892, 1154).—The authors show that from the solubility of silver chloride in ammonia solution it is unsafe to deduce the exact composition of the dissolved molecular compound, although the results can be used to ascertain whether it is  $(\text{AgCl})_m, (m+1)\text{NH}_3$ . From the results with pure solutions of ammonia, it has been found that this formula does represent the molecular compound, but the value of  $m$  could not be calculated. Potassium chloride or silver nitrate in the ammonia solution depresses the solubility of the silver chloride, and from the depressions found it has been

calculated that the molecular compound,  $\text{AgCl} \cdot 2\text{NH}_3$ , is formed in solution. Similar experiments in ammonia solution were made with silver bromide, and it was shown that the corresponding compound,  $\text{AgBr} \cdot 2\text{NH}_3$ , is produced.

The *E.M.F.* of the concentration cells :

Silver | silver chloride in ammonia solution | ammonia solution | silver.

Silver | silver bromide in ammonia solution | ammonia solution | silver

in which the concentration of silver salt and ammonia varied, were determined. From the results obtained, it is proved that the cation present in the solution is  $\text{Ag}(\text{NH}_3)_2$ . The dissociation constant of the complex cation is very small,  $7.88 \times 10^{-8}$ , nevertheless excess of ammonia is required to prevent the dissociation in order that the silver chloride may be completely dissolved.

When equal quantities of 0.1*N* silver nitrate and 0.2*N* ammonia solutions are mixed, then of the silver present only 0.068 per cent. exists in the form of free ions. The electro-affinity (Abstr., 1899, ii, 542) of the silver is considerably increased by the addition of the neutral ammonia molecules.

J. McC.

**Chemical Equilibria between Acid Salts and Sparingly Soluble Salts.** By GAETANO MAGNANINI *Gazzetta*, 1901, 31, ii, 542—549.—[With CARLO GRIMALDI.]—A number of experiments have been made by placing mixtures of different salts and solutions in flasks which were then hermetically closed and shaken in a thermostat until equilibrium was reached, when the contents were examined. The salts employed comprised potassium hydrogen tartrate, potassium hydrogen oxalate, potassium hydrogen sulphate, and calcium sulphate, tartrate and hydrogen phosphate. The experiments are being continued, and will be discussed in a later paper.

T. H. P.

**Barium Sulphate as a Reagent for Colloidal Metallic Solutions.** By LUDWIG VANINO (*Ber.*, 1902, 35, 662—663).—The colour of colloidal solutions of metallic silver or gold, or of arsenious sulphide is at once removed by shaking with barium sulphate; dissolved colouring matters, for example gentianin or magenta, are, however, not eliminated under similar treatment.

W. A. D.

**Nature and Properties of Colloids.** By P. D. ZACHARIAS (*Zeit. physikal. Chem.*, 1902, 39, 468—484).—The paper contains an account of the views of the author regarding colloids and their properties. He considers the colloidal state to be always somewhat unstable and to always tend to the formation of a more stable form, the crystalline. The molecules are in general very great, and probably on this account less amenable to the action of crystallisation forces and more liable to associate and to form great molecular complexes. The absorption of water or other liquid into these complexes eventually results in the formation of a colloidal solution, a labile structure from which the dissolved substance may slowly separate. The formation of such solutions and of jellies is greatly favoured by the membraniform

structure of the molecules. The jelly consists of a molecular network in which microscopic spaces may exist, the seat of many absorption phenomena. He considers that colloids deserve much greater attention than they have hitherto received from chemical investigators.

L. M. J.

**The Nature of Radicles.** By DANIEL VORLÄNDER (*Annalen*, 1902, 320, 99—121).—Numerous examples in recent chemical literature go to show that the electrochemical state of elementary and compound radicles is not constant; it depends on the compound in which the radicles are found and may be either positive or negative.

The supposition that unsaturated radicles always have a negative character leads to much confusion, and is, moreover, opposed to the facts of experiments, for under certain conditions the introduction of unsaturated radicles enhances the basic nature of a compound. The unsaturated groups—phenyl, cyanogen, nitrosyl, and carbonyl are generally compared with the electronegative halogen atoms, but they have a capacity for inducing reaction which is absent in these elementary radicles. The state of saturation of a radicle is an empirical property, quite distinct from the electrochemical condition of the atom or groups of atoms.

A table is given showing that the mobility of hydrogen in certain organic compounds depends on its association with carbon atoms attached to unsaturated radicles; this element is much more firmly held when the carbon atom is combined with saturated radicles of electronegative character. The lability of chlorine and other non-metallic radicles is similarly dependent on the presence of unsaturated groups.

This connection between reactivity and unsaturated character is also noticeable among inorganic substances. Ammonia, which contains two free nitrogen valencies, is more reactive than ammonium chloride. The lower oxy-acids of chlorine, sulphur, and nitrogen are more reactive than the corresponding fully-oxidised compounds. Nitrous and sulphurous acids, for example, are each considered to contain two free valencies, which are satisfied by oxygen in nitric and sulphuric acids. The contrast between the inert character of phosphoric acid and the reactivity of the lower oxy-acids of phosphorus is explained by supposing that phosphorous and hypophosphorous acids possess the symmetrical and dihydroxylic formulæ respectively, and that therefore they each contain tervalent phosphorus with two free valencies.

A different degree of saturation is manifested when a straight chain unsaturated compound changes into a ring system.

The chemical reactivity of a substance may be compared with a change of electricity distributed over the surface of an insulated conductor. When the body is spherical the change is uniformly distributed and is in a comparatively stable condition; this arrangement is analogous with the state of a saturated compound. If the sphere is deformed, or if a portion of its surface is drawn out to a point, the distribution of the charge is altered, the density being greatest at the angular point where the electricity is most readily discharged; this condition

may be compared with that of an unsaturated compound, the points where the electrical density is greatest corresponding with the double linking of the molecule.

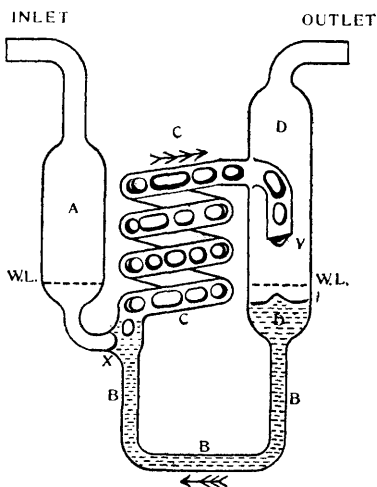
A symmetrical distribution of points on the electrified sphere leads to a state of comparatively great stability; this condition may be taken as typical of benzene and its homologues. The symmetrical arrangement being impossible with the di- and tetra-hydrobenzenes, these compounds are very labile and unsaturated. If the quantity of electricity is constant, the density depends on the superficial area of the charged body; a small sphere is more readily discharged than a large one. The electrical analogy supplies an explanation of the fact that polymerides are less reactive than their generators.

The difference of potential of two charged bodies depends on the medium between them, and, in an analogous manner, the reactivity of compounds varies with the solvent employed in carrying out their condensations.

G. T. M.

**Chemical Gas Washing Apparatus.** By C. E. STROMEYER, (*Mem. Manchester Phil. Soc.*, 1902, 46, [viii], 1—3).—The figure shows the form of the apparatus, which was devised for dealing with large quantities of gas and small amounts of absorbing liquid. The liquid is carried along between the gas bubbles through the coil C. The internal diameter of the tube C should be about  $\frac{1}{8}$  inch, and its length about 30 inches.

J. McC.





### Inorganic Chemistry.

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**Action of Chromic Acid on Hydrogen Peroxide.** By A. BACH (*Ber.*, 1902, 35, 872—877).—In absence of an acid, chromic acid in aqueous solution liberates the whole of the active oxygen of hydrogen peroxide without being itself affected; when sulphuric acid is present, however, 1 mol. of chromic acid is used for every 2 mols. of hydrogen peroxide present, the action probably taking place according to the equation  $4\text{CrO}_3 + 8\text{H}_2\text{O}_2 + 6\text{H}_2\text{SO}_4 = 2\text{Cr}_2(\text{SO}_4)_3 + 7\text{O}_2 + 14\text{H}_2\text{O}$  (contrast Baumannn, *Abstr.*, 1891, 245). Traube's view that the hydrogen of hydrogen peroxide is oxidised to water by

potassium permanganate or silver oxide with liberation of the oxygen of the peroxide cannot be correct, for this would necessitate a reduction of chromic acid in neutral solution, and an interaction  $2\text{CrO}_3 + 3\text{H}_2\text{O}_2 + 3\text{H}_2\text{SO}_4 = \text{Cr}_2(\text{SO}_4)_3 + 3\text{O}_2 + 6\text{H}_2\text{O}$  in acid solution; Berthelot's view of the formation of an unstable hydrogen trioxide is also not in accord with a ratio  $\text{CrO}_3 : \text{H}_2\text{O}_2 = 2 : 1$ . It is more probable that an unstable additive compound of hydrogen peroxide and chromic acid is formed, which decomposes spontaneously in neutral solution with regeneration of chromic acid, although in acid solution a reduction of the latter occurs.

W. A. D.

**Relative Strength of Hydrochloric and Nitric Acids.** By OTTO KÜHLING (*Ber.*, 1902, 35, 678—680).—A reply to the criticisms of Sackur and Bodländer (this vol., ii, 204).

T. M. L.

**Conversion of Orthoperiodic Acid into Normal Periodic Acid.** By ARTHUR B. LAMB (*Amer. Chem. J.*, 1902, 27, 134—138).—When heated at  $100^\circ$  under a pressure of 12 mm. orthoperiodic acid loses water to the extent of 15.62 per cent. This corresponds with the formation of periodic acid of the formula  $\text{HIO}_4$ . The amount of iodine liberated from potassium iodide also shows that  $\text{HIO}_4$  had been produced. By heating to a higher temperature it is not possible to obtain the heptoxide ( $\text{I}_2\text{O}_7$ ), for decomposition takes place with formation of the pentoxide.

J. McC.

**Formation of Ozone by the Electric Discharge.** By ALEXANDRE DE HEMPTINNE (*Bull. Acad. Roy. Belg.*, 1901, 612—621. Compare Abstr., 1898, i, 461).—The author has studied the formation of ozone by means of the electric discharge and finds that the amount of that gas produced varies greatly with the distance of the tin-foil plates from one another, and with their size. It is not proportional to the amount of air passed in a given time, and the pressure has apparently little influence. The intensity of the electrical current has also a very considerable influence on the amount of ozone formed, a current of low potential and high density being more advantageous than one of high potential. For a given value of electrical energy, there will be a given value of those different factors for which the formation of ozone is a maximum. The increase in the amount of ozone by employing oxygen instead of air is not sufficient to justify its use from an economic standpoint.

A. F.

**Physical Chemistry of Sulphuric Acid.** By OTTO SACKUR (*Zeit. Elektrochem.*, 1902, 8, 77—82).—A critical *résumé* of recent papers by Knietzsch (this vol., ii, 132), Schenck (Abstr., 1901, ii, 380), Oddo (Abstr., 1901, ii, 650), and others. In explanation of the fact that sulphuric acid containing 98 per cent. of  $\text{H}_2\text{SO}_4$  absorbs sulphur trioxide better than acid of any other concentration, it is assumed that the equilibrium  $2\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O} + \text{SO}_3$  is established in this acid; a stronger acid will contain more free sulphur trioxide, and the partial pressure of this substance in its vapour will be greater; it will therefore absorb it less readily. A weaker acid will contain uncom-

bined water, in contact with which the unimolecular  $\text{SO}_3$  will rapidly polymerise to bimolecular  $\text{S}_2\text{O}_6$ , which is very slowly absorbed by sulphuric acid. The hypothesis also offers a plausible explanation of the peculiarities in the physical properties of this acid. T. E.

**Action of Hydrogen on Sulphides and Selenides.** By HENRI PELABON (*Ann. Chim. Phys.*, 1902, [vii], 25, 365—432).—The greater portion of this communication relates to work already published (compare Abstr., 1898, ii, 568; 1899, ii, 24; 1900, ii, 346, 352, 652; 1901, ii, 165, 313, 545, 656). Silver readily attacks hydrogen selenide, and when in excess decomposes it entirely; on the other hand, the action of hydrogen on heated silver selenide is very slight, even at  $620^\circ$  the decomposition is inconsiderable, and after 48 hours the ratio of gaseous hydride to total hydrogen is only 1.01. Hydrogen has a very appreciable action on arsenious selenide,  $\text{As}_2\text{Se}_3$ , even at  $440^\circ$ , and when excess of the selenide is employed the limiting value of the characteristic ratio is 7.9; at  $610^\circ$  this value increases to 13.5. The interaction of hydrogen with mixtures of selenium and arsenic at  $610^\circ$  decreases rapidly as the proportion of the latter metalloid increases. Bismuth selenide,  $\text{BiSe}$ , obtained by fusing together its constituents in equivalent proportions, is slightly decomposed by hydrogen at  $610^\circ$ , but the change is limited by the inverse action; the characteristic ratio is 3.34, but this value rapidly diminishes to zero as the amount of bismuth is increased. The relations between the characteristic ratio and the temperature are indicated by curves. G. T. M.

**Physical Properties of Hydrogen Selenide.** By ROBERT DE FORCRAND and HENRI FONZES-DIACON (*Compt. rend.*, 1902, 134, 171—173. Compare Abstr., 1900, ii, 405).—Hydrogen selenide is liquefied and even solidified by a freezing mixture of carbon dioxide, snow, and methyl chloride; it melts at  $-64^\circ$ , and boils at  $-42^\circ$  under 760 mm. pressure; the sp. gr. of the liquid at its boiling point is 2.12. The solubility coefficients of the gas in water at  $4^\circ$ ,  $9^\circ$ ,  $13.2^\circ$ , and  $22.5^\circ$  are 3.77, 3.43, 3.31 and 2.70 vols. respectively. Pure hydrogen selenide decomposes very slowly; a sample collected over mercury and exposed to light contained only 15 per cent. of hydrogen at the end of seven days. G. T. M.

**Vapour Tensions of Hydrogen Selenide and the Dissociation of its Hydrate.** By ROBERT DE FORCRAND and HENRI FONZES-DIACON (*Compt. rend.*, 1902, 34, 229—231).—The following four points on the vapour pressure curve were determined,  $-42^\circ$ , 1 atms.;  $-30^\circ$ , 1.75 atms.;  $0.2^\circ$ , 4.5 atms.;  $30.8^\circ$ , 12 atms. From these values by Clapeyron's formula, the molecular heat of vaporisation is calculated to be 4740 cal., and hence the Trouton constant is  $4740/231 = 20.5$ , indicating the absence of polymerisation. The hydrate was obtained in the form of colourless crystals, and the following vapour pressures were found:  $-0^\circ$ , 346 mm.;  $2.35^\circ$ , 432 mm.;  $3.40^\circ$ , 490 mm.;  $5.40^\circ$ , 597 mm.;  $7.50^\circ$ , 718 mm.;  $14.1^\circ$ , 1.9 atms.;  $22^\circ$ , 5 atms.;  $30^\circ$ , 11 atms. Above  $30^\circ$ , the hydrate does not exist. From these values the heat of formation of the solid hydrate is calculated to be 16820 cal. L. M. J.

**Comparison of the Properties of Hydrogen Selenide and Hydrogen Sulphide.** By ROBERT DE FORCRAND and HENRI FONZES-DIACON (*Compt. rend.*, 1902, 134, 281—283. Compare preceding abstract).—Hydrogen sulphide melts at  $-86^{\circ}$  and boils at  $-61^{\circ}$  under 773 mm. pressure. The latter number agrees with Regnault's determination,  $-61.6^{\circ}$  under 760 mm. pressure, but not with Faraday's,  $-73^{\circ}$ .

In the following table, the properties of hydrogen sulphide and hydrogen selenide are compared :

	H <sub>2</sub> S.	H <sub>2</sub> Se.
Boiling point under 760 mm., $T$ (absolute) .....	211.4°	231°
Critical temperature, $T_c$ (absolute) .....	373.2°	410°
$T/T_c$ .....	0.566	0.564
Critical pressure (in atmospheres).....	92	91
Melting point .....	187°	209°
Density of liquid at boiling point, $D$ .....	0.86	2.12
Molecular volume of liquid, $PM/D$ .....	39.53	38.11
Heat of volatilisation (in calories), $L$ .....	4230	4740
$L/T$ (Trouton's number) .....	20.01	20.52
Heat of formation of hydrate (in calories) .....	16340	16820
Temperature (absolute) at which vapour pressure of hydrate attains 760 mm. ....	273.35°	281°
Solubility in water at $4^{\circ}$ (in volumes) .....	4.04	3.77
„ „ 22.5° .....	2.75	2.70

A comparison of the properties of hydrogen sulphide or hydrogen selenide with those of water shows a considerable dissimilarity.

K. J. P. O.

**Atomic Weight of Tellurium.** By ALEXANDER GUTBIER (*Annalen*, 1902, 320, 52—65. Compare Abstr., 1901, ii, 501).—The atomic weight of tellurium is determined by treating an aqueous solution of crystallised telluric acid or a hydrochloric acid solution of tellurium dioxide with hydrazine hydrate, the reduction being performed in an atmosphere of hydrogen. The precipitated tellurium is very readily oxidised ; it is rapidly washed with water and dried by warming in a current of hydrogen. The mean values obtained from telluric acid and tellurium dioxide are 127.34 (3 expts.) and 127.55 (3 expts.) respectively when  $O=16$  ; the constant obtained by estimating the water in crystallised telluric acid is 127.65 (2 expts.). The final result calculated from the three series of experiments is 127.51 (compare this vol., ii, 67, 69). The communication concludes with a criticism of Steiner's method of determining this atomic weight (compare Abstr., 1901, ii, 236).

G. T. M.

**Some Nitrogen Compounds.** By ANGELO ANGELI and FRANCESCO ANGELICO (*Atti R. Accad. Lincei*, 1901, [v], 10, ii, 303—307).—When solutions of hydroxylamine sulphate and of Caro's acid, neutralised with potassium carbonate, are allowed to interact in the cold, the liquid assumes an acid reaction and after a time ceases to reduce Fehling's solution. Also, when treated with aldehydes, the liquid

gives a vigorous reaction for hydroxamic acid, and hence it probably contains the residue,  $\text{NOH}$ , or its hydrate,  $\text{NH}(\text{OH})_2$ .

T. H. P.

**Neutralisation of Phosphoric Acid.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1902, [vii], 25, 145—153).—A detailed account of work already published (compare Abstr., 1901, ii, 502).

G. T. M.

**Reactions of two Basic Oxides Exposed Simultaneously to the Action of Phosphoric Acid.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1902, [vii], 25, 153—163).—A detailed account of work already published (compare Abstr., 1901, ii, 504).

G. T. M.

**Phosphoric Acid and Chlorides of the Alkaline Earths.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1902, [vii], 25, 176—196. Compare Abstr., 1901, ii, 551).—A detailed account of work already published.

G. T. M.

**Simple Apparatus for Demonstrating the Manufacture of Water Gas.** By C. E. WATERS (*Amer. Chem. J.*, 1902, 27, 139—142).—The author describes a simple apparatus in which the "producer" consists of a wide iron tube. This contains a fuse of loosely twisted cotton string round which the coke is packed. The fuse is lighted and oxygen blown in at the bottom until the coke is hot. Superheated steam then enters by a side tube near the bottom of the producer, and water gas issues at the top and may be collected over water.

J. McC.

**Action of some Reagents on Amorphous Silicon.** By PAUL LEBEAU (*Bull. Soc. Chim.*, 1902, [iii], 27, 42—44).—Amorphous silicon, even when finely divided, is not attacked by solutions of cupric chloride, cupric sulphate, cupric chloride and ammonium chloride, cupric chloride and potassium chloride, chromic acid, or nitric acid diluted with its own volume of water (compare Vigouroux, Abstr., 1895, ii, 263), which are the reagents generally employed for acting on cast iron and steel. The absence of silicon from the products of action of these reagents on the latter substances shows that it is present in them in combination and not in the free state.

A. F.

**Heptahydrate of Sodium Sulphate.** By LOUIS C. DE COPPET (*Chem. Centr.*, 1902, i, 397; from *Bull. Soc. Vaud. Sci. nat.*, 1901, 37, 455—462).—The original paper contains a description of experiments which show that the change in the crystalline form of the heptahydrate of sodium sulphate which takes place when the crystals are stirred with the mother liquor and the latter allowed to solidify is not due to the crystallisation of the mother liquor enclosed in the crystals. The crystals of the heptahydrate are destroyed in a few minutes by contact with the smallest quantity of the decahydrate or of the anhydrous salt obtained from it by exposure to the air. The change from

heptahydrate into decahydrate and the anhydrous salt is accompanied by the development of a considerable amount of heat. According to the author, this change is possible at the ordinary temperature although of infrequent occurrence, but at lower temperatures it probably cannot take place except through the agency of the decahydrate. The anhydrous sodium sulphate, obtained by the efflorescence of the heptahydrate, has properties which differ from those of the anhydrous salts already described by the author, hence, including Wyruboff's salts, the anhydrous salt has been prepared in six different forms.

E. W. W.

**Physico-chemical Properties of Sodium Thiosulphate.** By FRANZ FAKTOR (*Chem. Centr.*, 1902, i, 164—165; from *Pharm. Post*, 34, 769—770. Compare this vol., ii, 25).—Determinations of the molecular weight of sodium thiosulphate by the depression of the freezing point of solutions gave 59·92 and 60·5, whilst by the boiling point method the values 78·4, 79·2, and 77·9 were obtained, hence at low temperatures the salt forms the ions  $\text{Na}_2\text{Na}$  and  $\text{S}_2\text{O}_3$ , but at higher temperatures it is decomposed into the ions  $\text{Na}$  and  $\text{NaS}_2\text{O}_3$ . Determinations of the electric conductivity of solutions of sodium thiosulphate of different concentrations also show that ionisation takes place in the stages  $\text{Na}_2\text{NaS}_2\text{O}_3$  and  $\text{Na}_2\text{Na}_2\text{S}_2\text{O}_3$ , and that the salt is hydrolysed in aqueous solutions. The last conclusion is also confirmed by experiments on the inversion of sugar. When electrolysed, sodium thiosulphate forms sulphur, hydrogen sulphide, tetrathionic acid, sulphur dioxide, and sulphuric acid.

E. W. W.

**Formation of Insoluble Phosphates by Double Decomposition: Disodium Phosphate and Silver Nitrate.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1902, [vii], 25, 164—176).—An account of work already published (*Abstr.*, 1901, ii, 503).

G. T. M.

**Lithium Antimonide and some other Alloys of Lithium.** By PAUL LEBEAU (*Compt. rend.*, 1902, 134, 231—233).—Lithium and antimony combine directly with great violence, but it was not found possible to obtain a definite compound in this way. If, however, a fused mixture of equal parts of lithium and potassium chlorides is electrolysed with a current of 15 amperes, using an antimony cathode, *lithium antimonide*,  $\text{SbLi}_3$ , is readily obtained as a dark grey substance with a crystalline texture; it readily decomposes water, liberating pure hydrogen. Its melting point is higher than those of its constituents, and its properties will be described later.

The method employed for the preparation of the antimonide is somewhat widely applicable, and alloys of lithium with tin and lead have been obtained in the same way.

C. H. B.

**Action of Lithium-Ammonium on Antimony, and the Properties of Lithium Antimonide.** By PAUL LEBEAU (*Compt. rend.*, 1902, 134, 284—286. Compare preceding abstract).—Lithium antimonide,  $\text{SbLi}_3$ , is formed when a small fragment of antimony is

heated with lithium in a sealed tube containing liquid ammonia; the reaction is completed when the blue colour of the lithium ammonium disappears; or finely powdered antimony may be suspended in liquid ammonia at  $-80^{\circ}$ , and lithium added in successive small portions until a permanent blue coloration is obtained. Lithium antimonide, thus prepared, is a brownish-grey powder in a very fine state of division, having a density 3.2 at  $17^{\circ}$ . It fuses a little above  $950^{\circ}$ , and is therefore less fusible than either of its components. It reacts readily with chlorine, bromine, iodine, sulphur, selenium or tellurium, and burns in oxygen with a violet flame. When heated with arsenic, it yields lithium arsenide. It is more easily decomposed by carbon than the corresponding arsenide. It decomposes hydrogen chloride, bromide, and iodide, the oxides of nitrogen, and sulphur dioxide with incandescence. At a red heat, ammonia is decomposed, hydrogen being evolved. The antimonide dissolves in liquid ammonia, forming a reddish-brown liquid which contains a *compound*,  $\text{LiSb}_3\text{NH}_3$ . With water, the antimonide reacts at the ordinary temperature, pure hydrogen being evolved, and antimony being formed as a black, flocculent mass; with aqueous acids, a little hydrogen antimonide is also formed. The chlorides, sulphides, and oxides of the metals are reduced by the antimonide.

K. J. P. O.

**Properties of Fused Calcium Oxide.** By HENRI MOISSAN (*Compt. rend.*, 1902, 134, 136—142).—It is not possible to melt pure lime by means of a blowpipe fed by detonating mixtures of hydrogen, acetylene, or carbon monoxide with oxygen; the oxide is, however, fused in an electric arc of 300 amperes and 50—70 volts; with 1000 amperes, fusion and vaporisation proceed simultaneously. The cubical and prismatic crystals found in the cooler parts of the furnace are colourless, transparent, and isotropic; the acicular prisms are, in reality, aggregates of small, superposed cubes, and this crystalline form of the oxide apparently belongs to the cubic system. These crystals, when embedded in Canada balsam, slowly break up into transparent anisotropic fragments, a result which indicates that crystalline calcium oxide is dimorphous. The sp. gr. of the crystallised oxide is 3.40, whilst that of the amorphous variety prepared from marble is 3.30.

The heats of neutralisation of the amorphous and crystalline modifications are identical (compare Gautier, *Abstr.*, 1899, ii, 399). Graphite, when immersed in fused lime, reduces the oxide with the formation of calcium carbide and carbon monoxide; in the presence of excess of the oxide, the carbide is decomposed, carbon monoxide and calcium vapour being evolved in accordance with the following equation,  $\text{CaC}_2 + 2\text{CaO} = 2\text{CO} + 3\text{Ca}$ . Silicon, titanium, and boron, when heated in melted lime, yield respectively calcium silicate, titanate, and borate; boron also gives rise to calcium boride,  $\text{CaB}_6$  (*Abstr.*, 1898, ii, 116). The metals of the iron group, chromium, manganese, iron, cobalt, and nickel, are oxidised by the fused lime, manganese being converted into manganous oxide, whilst chromium is present as the double oxide,  $\text{Cr}_2\text{O}_3, 4\text{CaO}$ ; traces of chromate are also found owing to the intervention of atmospheric oxygen. All these metals, excepting chromium, when heated in this manner are partially

volatilised, this phenomenon being especially noticeable in the case of manganese. Platinum, when mixed with fused calcium oxide, melts and partly volatilises; that portion of the metal which remains unvolatilised contains 2 or 3 per cent. of calcium. G. T. M.

**Calcium Carbophosphate.** By A. BARILLÉ (*Bied. Centr.*, 1902, 31, 136—137; From *Rép. Pharm.*, 1901, 145).—When dicalcium phosphate suspended in water is heated with carbon dioxide under pressure (13 kilos.), 25 to 50 per cent. dissolves according to the duration of the action. The solution, when exposed to air, deposits crystals of pure dicalcium phosphate. Calcium phosphate similarly treated dissolves to a less extent (10—25 per cent.), and the solution deposits a mixture of dicalcium phosphate and calcium carbonate (1 mol.  $P_2O_5$  to 3 mols.  $CaO$ ).

The author supposes that an unstable carbophosphate of the formula  $H_2Ca_2P_2O_8 \cdot 2CO_2$  is formed, but all attempts to isolate the substance failed. Dry carbon dioxide does not act on dry calcium phosphate. N. H. J. M.

**Chemical Equilibria: Ammonium Phosphates and Barium Chloride.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1902, [vii], 25, 197—200).—Monoammonium phosphate in dilute solution does not give precipitates with  $\frac{1}{2}$ , 1, or  $1\frac{1}{2}$  mols. of barium chloride even after several days; the liquid containing these substances is neutral to methyl-orange but acid to litmus or phenolphthalein. Diammonium phosphate gives precipitates with the preceding proportions of barium chloride, and the filtered solution is alkaline to methyl-orange and litmus, but acid to phenolphthalein, and in the last case when the liquid is neutralised with ammonia a slight precipitate is produced. When the solution remains for some time in contact with the precipitate, it becomes more nearly neutral to the three indicators; this change is more marked when the amount of barium salt is considerable.

Triammonium phosphate precipitates 1 atomic proportion of barium from the solution of its chloride; the filtrate is alkaline to the three indicators, and its alkalinity is unaltered when left in contact with the insoluble barium phosphate for 2 days, showing that the precipitation is immediate and complete. When  $1\frac{1}{2}$  mols. of the barium salt are employed, the values obtained on titration vary with the time during which the solution remains in contact with the precipitate. G. T. M.

**Chemical Equilibria: Ammonium Phosphate and Magnesium Chloride.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1902, [vii], 25, 200—204. Compare preceding abstract).—The filtrate obtained from a mixture of phosphoric acid, magnesium chloride, and ammonia in dilute solution is alkaline towards methyl-orange, the alkalinity of the rapidly filtered solution varying considerably when the order of mixing is changed. The filtrate is acid to phenolphthalein, the amount of acidity depending on the order of mixing. The greatest departure from neutrality is obtained when the



magnesium chloride (1 mol.) is added to the solution containing phosphoric acid (1 mol.) and ammonia (2 mols.). After 28 hours' contact with the precipitate, the liquid attains a state of equilibrium which is independent of the order of mixing. When the proportion of ammonia is increased to 3 mols., the filtrate still gives the preceding reactions with the indicators, but the variation due to time and order of mixing is far less appreciable; the alkalinity towards methyl-orange is less than in the preceding experiment, although the amount of ammonia present is actually greater; this result is due to the formation of magnesium ammonium phosphate.

G. T. M.

#### Thermal Study of some Alloys. Zinc and Aluminium.

By WLADIMIR F. LUGININ and A. SCHUKAREFF (*Arch. Sci. phys. nat.*, 1902, [iv], 13, 5—29).—The authors have attempted to find the heat of formation of a number of zinc-aluminium alloys, in definite proportions, by the determination of the difference of the heats of dissolution in dilute hydrochloric acid, of the alloy, and the mixed metals. The acid employed was of the strength represented by  $\text{HCl}, 10\text{H}_2\text{O}$ , and it was first proved that the products of dissolution were identical in the two cases. The apparatus employed is fully described and the results obtained for the heat of formation of 1 gram of the alloy are:  $\text{Al}_5\text{Zn}$ ,  $-131.7$  cal.;  $\text{Al}_4\text{Zn}$ ,  $-5.0$  cal.;  $\text{Al}_3\text{Zn}$ ,  $+1.4$  cal.;  $\text{Al}_2\text{Zn}$ ,  $+23.4$  cal.;  $\text{AlZn}$ ,  $+9.1$  cal.;  $\text{Al}_2\text{Zn}_3$ ,  $+2.3$  cal.;  $\text{AlZn}_2$ ,  $-4.0$  cal.;  $\text{AlZn}_3$ ,  $+15.2$  cal.; the positive sign indicates development of heat. In no case except the first is the thermal change sufficiently great as to be depended on, and no definite compound of zinc and aluminium is hence indicated.

L. M. J.

**Distillation of Metals and Distilled Metals.** By GEORG W. A. KAHLBAUM, KARL ROTH, and PHILIPP SIEDLER (*Zeit. anorg. Chem.*, 1902, 29, 177—294).—In order to obtain metals in a high state of purity, a number of these have been distilled at low pressure, using the continuous automatic mercury pump previously described by Kahlbaum (*Abstr.*, 1894, ii, 349) and the volumeter of McLeod as modified by Kahlbaum (*Zeit. Instrumentenkunde*, 1895, 191). The distillation was carried out in porcelain tubes, three forms of which have been used. The course of the distillation was followed by taking photographs, by means of Röntgen rays, of the porcelain tubes. The porcelain is transparent to these rays, but the metals are opaque. The purification of tellurium by distillation was examined by observation of the spectrum of the distilled element and it was found that successive distillations remove lines from the spectrum.

The following metals have been distilled and their specific gravities, specific heats, and crystalline forms determined: copper, silver, gold, lead, zinc, cadmium, tellurium, antimony, and bismuth. The specific gravity was determined by a pycnometric method, and the specific heat by a Bunsen calorimeter. The compressibility of the metals was also determined as well as the specific gravity after the pressure had been applied. The results obtained were:

	Cryst. form.	$d\ 20^{\circ}/4$	Sp. ht.
Copper .....	Cubic	8.93258	0.09272
Copper, pressed (10,000 atmos.)		8.93764	0.09266
Silver .....	Cubic	10.4923	0.05608
Silver, pressed .....		10.5034	0.05623
Gold .....	Cubic	18.8840	0.0309
Gold, pressed.....		19.2685	0.03087
Lead .....	Cubic	11.3415	0.03053
Lead, pressed.....		11.3470	0.03083
Zinc .....	Rhombohedral (?)	6.9225	0.0939
Zinc, pressed .....		7.12722	0.0940
Cadmium .....	Rhombohedral	8.64819	0.0559
Cadmium, pressed .....		8.64766	0.0560
Tellurium .....	Rhombohedral	6.23538	0.04878
Antimony .....	Rhombohedral	6.61781	0.04973
Antimony, pressed .....		6.69090	0.04957
Bismuth .....		9.78143	0.03055

In the hope of finding a heavy liquid suitable for the specific gravity determinations, the authors examined solutions of barium borotungstate and the corresponding salts of cadmium (Klein's solution), copper, cobalt, nickel, and uranium and of thallium ethoxide and some other thallium alkyl oxides. The densities of the solutions were:

Copper borotungstate .....	$d\ 15.8^{\circ}/4^{\circ}$	3.0085
Cobalt borotungstate .....	$d\ 19.2/4$	3.1369
Nickel borotungstate .....	$d\ 15.9/4$	2.2956
Uranium borotungstate .....	$d\ 20.8/4$	1.9442
Cadmium borotungstate .....	$d\ 16.2/4$	3.2868
Thallium ethoxide .....	$d\ 0/4$	3.562
„ „ .....	$d\ 20/4$	3.522

The refractive and dispersive powers of the solutions have also been determined: the value of  $n_{\text{Na}}^{20^{\circ}}$  for saturated cobalt borotungstate is 1.5981, and the dispersion  $\Delta = 0.0123$ ; for the copper salt,  $\Delta = 0.0134$ ; for the nickel salt,  $n_{\text{Na}}^{20^{\circ}} = 1.4945$ ,  $\Delta = 0.0102$ ; for the cadmium salt,  $n_{\text{Na}}^{20^{\circ}} = 1.5836$ ,  $\Delta = 0.0144$ ; for the uranium salt,  $n_{\text{Na}}^{20^{\circ}} = 1.4573$ ,  $\Delta = 0.0075$ ; and for thallium ethoxide,  $n_{\text{Na}}^{20^{\circ}} = 1.6826$ , and  $\Delta = 0.0286$ .

None of the solutions could be used in the investigation.

J. McC.

**Alloys of Lead and Tellurium.** By HENRY FAY and C. B. GILLSON (*Amer. Chem. J.*, 1902, 27, 81—95).—The freezing points of alloys of lead and tellurium were determined by means of a Le Chatelier pyrometer. The results are tabulated in the original.

The composition of the alloy of maximum freezing point corresponds with the proportions of the metals in lead telluride, PbTe. Lead easily becomes supersaturated with respect to lead telluride, which separates out at the higher freezing point, and the lower freezing point then corresponds with the solidification of the lead. When still

more tellurium is present, lead telluride again separates at the higher temperature, but the lower freezing point corresponds with the complete solidification of the alloy, which is an eutectic of lead telluride and tellurium.

The microstructure of the alloys has been examined; the eutectic can always be seen interspersed between the crystals of lead or tellurium, according to which of these is present in excess.

The hardness of the alloy increases with the amount of tellurium present. The alloys containing more than 50 per cent. of tellurium are very brittle. J. McC.

**Radioactive Lead.** By KARL A. HOFMANN and V. WÖFL (Ber., 1902, 35, 692—694).—A very highly radioactive sulphide can be prepared from pitchblende by heating the lead sulphate with potassium hydroxide and hydrazine sulphate, evaporating with hydrochloric acid and chlorine water, extracting with dilute hydrochloric acid, and precipitating with hydrogen sulphide. The active material differs from bismuth-polonium, radium, and actinium, and reacts similarly to lead. When the sulphide is converted into sulphate, a small amount of active material can be extracted with dilute sulphuric acid, but the residue is also strongly active. Measurements were made of the times required to discharge an electrometer in presence of the different materials.

T. M. L.

**Analysis of Antique Metallic Articles.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1902, 134, 142—145).—A Chaldean statuette of the 26th century B.C. consists of 76—77.4 per cent. of copper, 17—18 per cent. of lead, and 2—6 per cent. of sulphur, with traces of iron; the composition of this specimen differs markedly from that of objects of a similar nature dating from the 22nd century B.C., the latter statuettes consisting of almost pure copper. Analyses of Babylonian statuettes of unknown date are also tabulated (compare Abstr., 1901, ii, 25, 318, 386, 615).

G. T. M.

**Constitution of Copper-Tin<sup>2</sup>Alloys.** By CHARLES T. HEYCOCK and FRANCIS H. NEVILLE (*Proc. Roy. Soc.*, 1902, 69, 320—329. Compare Abstr., 1901, 508).—The evidence obtained from a microscopic study of copper-tin alloys chilled at selected temperatures, combined with the results of pyrometric investigation, is interpreted on the basis of Roozeboom's theory of solid solutions. The conclusions thus arrived at are condensed in an equilibrium diagram, to which reference must be made for a full appreciation of the results. The solids which may be at one time or another, according to temperature and concentration, in contact with the liquid alloy, are (1), (2), and (3) mixed crystals of three types, (4) the compound  $\text{Cu}_3\text{Sn}$ , (5) the compound  $\text{CuSn}$ , and (6) pure tin. There is also a substance, supposed to be  $\text{Cu}_4\text{Sn}$ , which is not found in contact with the liquid.

J. C. P.

**Action of Cupric Hydroxide on Aqueous Solutions of Metallic Salts.** By AMABLE MAILHE (*Compt. rend.*, 1902, 134, 233—236. Compare Abstr., 1901, ii, 601, and this vol., ii, 140).—The action of cupric hydroxide on aqueous solutions of cupric, cobaltous,

nickel, and manganous nitrates yields crystalline double salts of the type  $M(NO_3)_2 \cdot 3CuO \cdot 3H_2O$ . In some cases, the blue hydroxide gives better results than the black hydroxide, and the action is accelerated by heating. Cadmium nitrate yields a compound not quite of the same type:  $Cd(NO_3)_2 \cdot CuO \cdot 5H_2O$ , whilst mercuric and lead nitrates give the basic nitrates  $Hg(NO_3)_2 \cdot HgO \cdot H_2O$ ;  $Pb(NO_3)_2 \cdot PbO \cdot H_2O$ . Iron (ferric) and aluminium are completely displaced from solutions of their nitrates by cupric hydroxide. C. H. B.

**Preparation of Metals of the Cerium Group by Electrolytic Fusion.** By WILHELM MUTHMANN, H. HOFER, and L. WEISS (*Annalen*, 1902, 320, 231—269).—The authors employ a jacketed copper crucible which can be cooled with water throughout the electrolysis. The electrodes are carbon rods, the cathode passing through the bottom of the crucible; the temperature is regulated by means of smaller carbon rods, 3 mm. in thickness, and 23 mm. in length, placed between the electrode terminals.

When a current of 40 amperes and 10—12 volts is employed with this apparatus, cryolite is readily melted, and on removing the connecting small carbon rods the electrolysis sets in, the current strength now being 8—10 amperes with 60—65 volts. Lead chloride is conveniently electrolysed with a current of 30—35 amperes and 8—10 volts.

Anhydrous cerous chloride, mixed with 10 per cent. of a mixture of sodium and potassium chlorides, is electrolysed with a current of 30—40 amperes and 12—15 volts; the metal isolated contains 99.92 per cent. of cerium. Cerium is only slightly oxidised in dry air; it slowly decomposes water in the cold, but more rapidly on heating. Nitric acid, even when moderately dilute, attacks cerium, yielding a brown hydroxide,  $H_2CeO_3$ , a substance which yields the dioxide on heating.

Neodymium is obtained when its chloride is electrolysed with a current of 56 amperes and 25 volts; barium chloride is added from time to time because this salt has the property of decreasing the conductivity of the fused mass, and in this way increasing the temperature. Neodymium is a silvery white metal, whilst cerium has an iron-grey colour. The former metal has the higher melting point, and is the more oxidisable; it decomposes water especially on warming and is attacked by all acids.

A mixture of cryolite and one of the oxides of cerium yields on electrolysis an alloy of cerium and aluminium. Cerium carbide,  $CeC_2$ , is obtained from the dioxide by electrolysis in the presence of carbon. This substance yields a mixture of acetylene and ethylene when treated with hydrochloric acid.

The remainder of the communication is devoted to the description of methods for obtaining derivatives of the cerium group of metals in a pure state; the memoir also contains four plates illustrating the electrolytic apparatus. G. T. M.

**New Method of separating Cerium from Mixtures of Rare Earths.** By RICHARD JOS. MEYER and M. KOSS (*Ber.*, 1902, 35, 672—678).—The complete separation of cerium from a mixture of rare earths can be readily effected by boiling with magnesium acetate, which precipitates quadrivalent cerium, but leaves the other earths

in solution; the precipitate is not quite pure, but is readily soluble in nitric acid, and can therefore be easily purified, if required, by precipitating the double salt with ammonium nitrate.

Ceric salts are precipitated quantitatively as a basic acetate by sodium acetate in a hot solution, but the precipitate dissolves again to some extent on cooling and must therefore be filtered while hot; didymium and lanthanum are not precipitated by this method, but didymium is always carried down with the cerium from a solution containing both elements. Cerium can be precipitated from a neutral solution of the nitrate by hydrogen peroxide and sodium acetate, but didymium is also thrown down when the hydrogen peroxide is in excess, although lanthanum remains entirely in solution; the method is not technically applicable to the separation of cerium, but may possibly serve for the separation of didymium from lanthanum.

The use of magnesium acetate overcomes most of the difficulties experienced with sodium acetate, and allows of a complete technical separation of cerium in one operation, the only impurity being 3 to 4 per cent. of didymium, which can readily be removed in a subsequent operation.

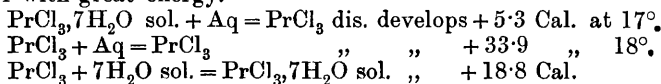
T. M. L.

**Action of Hypochlorous Acid on Praseodymium Dioxide.** By PETR. G. MELIKOFF and B. E. KLIMENKO (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 739—740. Compare this vol., ii, 140).—The action of hypochlorous acid on praseodymium dioxide gives rise to the evolution of oxygen and the formation of chloric acid. In this reaction, which proceeds very slowly in the cold, but much more energetically at higher temperatures, no ozone is given off, and any which is formed must be at once used up in oxidising the hypochlorous acid.

T. H. P.

**Praseodymium Chloride.** By CAMILLE MATIGNON (*Compt. rend.*, 1902, **134**, 427—429).—Hydrated praseodymium chloride,  $\text{PrCl}_3 \cdot 7\text{H}_2\text{O}$ , loses water slowly at the ordinary temperature in a dry atmosphere, and tends to produce a hydrate,  $\text{PrCl}_3 \cdot 3\text{H}_2\text{O}$ . If heated at  $115^\circ$ , it loses water and hydrogen chloride and is converted into an oxychloride. If, however, it is heated in a current of dry hydrogen chloride at  $108^\circ$ , it yields a new hydrate,  $\text{PrCl}_3 \cdot \text{H}_2\text{O}$ , and at  $185^\circ$  becomes anhydrous without formation of any oxychloride. The heptahydrate begins to melt at  $105^\circ$ , and loses water. It dissolves readily in water, and the solution saturated at  $13^\circ$  has sp. gr. 1.687 at  $16^\circ/4^\circ$ ; 100 parts contain 76.97 parts of the hydrated salt or 50.96 parts of the anhydrous salt. At  $100^\circ$ , the solubility in water is unlimited. In dilute hydrochloric acid, the solubility diminishes in accordance with Engel's law. A concentrated solution of the chloride dissolves praseodymium oxalate, and other oxalates of the rare metals, forming crystallisable oxalochlorides.

The anhydrous chloride melts at a red heat, forming a green liquid, which is not sensibly volatile at  $100^\circ$ . The salt combines with water with great energy.



The anhydrous chloride is very soluble in alcohol but is insoluble in ether and most organic liquids, or in inorganic chlorides such as phosphorus trichloride, or stannic chloride. C. H. B.

**Aluminium-Iron and Aluminium-Manganese Alloys.** By LÉON GUILLET (*Compt. rend.*, 1902, 134, 236—238).—When an intimate mixture of aluminium and ferric oxide is heated, the limit of inflammation corresponds with a mixture which should yield the alloy FeAl, but if the mixture is previously heated at 800° the limit of inflammation may be extended to the mixture yielding FeAl<sub>4</sub>. The product from mixtures between FeAl and Fe<sub>10</sub>Al rapidly falls to a powder containing tetrahedral crystals of the compound Fe<sub>2</sub>Al<sub>3</sub>, which seems to correspond with the maximum of the curve of fusibility. Products between FeAl<sub>2</sub> and FeAl<sub>4</sub> yield prismatic crystals, often 60 to 80 mm. long, of the compound FeAl<sub>3</sub>.

With aluminium and manganic oxide, the limit of inflammation corresponds with a mixture which should yield MnAl<sub>4</sub>, but by previous heating can be extended to the mixture which should yield MnAl<sub>6</sub>. There is, however, always considerable loss in the form of manganous oxide. Products between the limits MnAl<sub>3</sub> and MnAl<sub>2</sub> rapidly fall to powder containing crystals of the compound MnAl<sub>3</sub>, which can be isolated by treatment with dilute hydrochloric acid. Products between Mn<sub>2</sub>Al and Mn<sub>5</sub>Al behave similarly, but yield crystals of the compound Mn<sub>2</sub>Al<sub>3</sub>. A mixture of manganic oxide and aluminium in the proportions to form MnAl<sub>4</sub> yields a small quantity of this compound in filiform crystals in a mass of corundum. C. H. B.

**Cementation of Iron by Silicon.** By PAUL LEBEAU (*Bull. Soc. Chim.*, 1902, [iii], 27, 44—45).—By heating iron embedded in crystals of silicon at the temperature of a good forge, Moissan (Abstr., 1896, ii, 173) found that the two substances combined to form iron silicide. The author now shows that combination of the two elements takes place at a much lower temperature (950°), the process therefore resembling the cementation of iron by carbon. A. F.

**Crystallisation of Chromic Oxide.** By ALFRED DITTE (*Compt. rend.*, 1902, 134, 336—343).—It is well known that when a mixture of potassium dichromate and sodium chloride is heated to bright redness, a considerable quantity of chromic oxide is obtained crystallised in thin, brilliant plates, and the result is generally attributed to a dissolution of the chromic oxide in the fused sodium chloride. No similar result is obtained with potassium dichromate and potassium chloride, and direct experiment shows that amorphous chromic oxide does not become crystallised when fused with sodium chloride. On the other hand, the crystallised oxide is readily obtained by heating a mixture of sodium dichromate and sodium chloride. The explanation of the change, and of the different behaviour of potassium chloride, lies in the relatively high stability of potassium chlorochromate on the one hand, and the instability of the corresponding sodium salt on the other. When a dichromate is fused with sodium chloride, chromyl dichloride is produced, and it is the decomposition of this substance that yields

the crystallised chromic oxide. If potassium chloride is substituted for the sodium salt, only a small quantity of chromyl dichloride is produced owing to the comparative stability of the potassium chlorochromate, which is the primary product. C. H. B.

**Molybdenum Oxides.** By MARCEL GUICHARD (*Compt. rend.*, 1902, 134, 173—174. Compare Abstr., 1900, ii, 80, 658; 1901, ii, 659).—The researches of Klason (see Abstr., 1901, ii, 162, 163) and Bailhache indicate that there are at least five blue oxides of molybdenum. In all probability, however, these different oxides either correspond with the blue oxide prepared by the author, or are mixtures of this compound with molybdenum trioxide. G. T. M.

**Analysis of the Lower Oxides of Molybdenum and of Metallic Molybdenum.** By CARL FRIEDHEIM and M. K. HOFFMANN (*Ber.*, 1902, 35, 791—798).—Molybdenum dioxide ( $\text{MoO}_2$ ) can be very easily prepared in a perfectly pure state by a modification of Guichard's method; the trioxide, is heated in hydrogen at the boiling point of sulphur and the product, which is a mixture of dioxide and trioxide, heated to dull redness in dry hydrogen chloride, when the trioxide is converted into a volatile oxychloride, and is thus removed.

The amount of molybdenum dioxide in one of the soluble or insoluble lower oxides of molybdenum can readily be estimated by treating the oxide with excess of a 10 per cent. solution of ferric ammonium sulphate, when the dioxide is oxidised to trioxide. The ferrous salt thus produced is titrated with standard potassium permanganate. In the case of a soluble lower oxide of molybdenum, a known excess of acidified potassium permanganate may be directly added, the excess being estimated by standard oxalic acid.

Metallic molybdenum is similarly quantitatively converted into the trioxide by ferric sulphate and can thus be estimated.

The authors find that the known process for estimating molybdenum and molybdenum dioxide, which is based on the reduction of ammoniacal silver nitrate to metallic silver, yields good results when very dilute ammoniacal silver sulphate is employed. The precipitated silver is collected and washed with a 10 per cent. solution of ammonium nitrate, and is then dissolved in nitric acid and weighed as chloride or titrated with ammonium thiocyanate. K. J. P. O.

**Tungsten, Molybdenum, Uranium, and Titanium. III.** By ALFRED STAVENHAGEN and E. SCHUCHARD (*Ber.*, 1902, 35, 909—912. Compare Abstr., 1899, ii, 489; 1900, ii, 80).—The following alloys were prepared by the method of aluminium-reduction: WCo, WMo, MoU, MoFe, MoSb, UFe, UCo, UMn, TiFe, TiCo, TiCu, PbW, PbMo, FeBa, CrCoWMo, TiWMo, MoUCrTi, and FeMnU. T. M. L.

**Tin Sponge and Crystals formed by Electrolysis.** By W. PFANHAUSER, jr. (*Zeit. Elektrochem.*, 1902, 8, 41—43).—When solutions of stannous or stannic chloride of more than normal strength are electrolysed with a current density at the cathode exceeding 0.01 ampere per sq. cm., crystals of tin are deposited. With more dilute

solutions, spongy tin is formed, whilst small currents deposit coherent metal from the concentrated solutions.

T. E.

**Enantiotropy of Tin.** VII. By ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 4, 377—378. Compare Abstr., 1900, ii, 83, 212, 408; 1901, ii, 106, 244).—Analytical examination shows that the tin used by the author in his previous researches contains only the slightest traces of impurities.

J. C. P.

**Alloys of Antimony and Tellurium.** By HENRY FAY and HARRISON EVERETT ASHLEY (*Amer. Chem. J.*, 1902, 27, 95—105).—The freezing points of a series of antimony and tellurium alloys were determined by the Le Chatelier pyrometer, and the specific gravities were also determined.

The composition of the alloy with maximum freezing point corresponds with the formula  $\text{Sb}_2\text{Te}_3$ . The compound forms an eutectic alloy (containing 87 per cent. of tellurium, and melting at  $421^\circ$ ) with tellurium; it is isomorphous with antimony.

The specific gravities found for the alloys are of little value, for it was almost impossible to obtain them free from air cavities.

Under the microscope, the alloy containing 61.37 per cent of tellurium appeared absolutely uniform. When more tellurium is present, eutectic alloy and antimony telluride can both be clearly seen.

J. McC.

**Preparation of Tantalum in the Electric Furnace and its Properties.** By HENRI MOISSAN (*Compt. rend.*, 1902, 134, 211—215).—When tantalum pentoxide is mixed with somewhat less than the calculated quantity of sugar-carbon, and heated for not less than 10 minutes in the electric furnace with a current of 60 volts and 800 amperes, a fused mass of metallic tantalum is obtained, containing 0.5 to 2.5 per cent. of carbon. It is brittle, and has a crystal-line fracture; its sp. gr. is 12.79, which is considerably higher than that given by Berzelius or Rose. Finely powdered tantalum burns in fluorine at the ordinary temperature; in chlorine, it is attacked at  $150^\circ$ , and burns at about  $250^\circ$ ; in bromine vapour, it is attacked at a red heat, but not in iodine vapour even at  $600^\circ$ . It burns in oxygen at  $600^\circ$ , but is not affected by sulphur, selenium, or tellurium vapour at  $700^\circ$ , or by phosphorus or arsenic at their boiling points, or by nitrogen at  $1200^\circ$ . Hydrogen chloride attacks tantalum with liberation of hydrogen, but water vapour and hydrogen sulphide have little or no action at  $600^\circ$ . Ammonia is decomposed at a dull red heat, but the tantalum does not increase in weight. Tantalum shows very little tendency to combine with metals. It reduces sulphur dioxide and nitrous and nitric oxides with incandescence at about  $500^\circ$ , phosphorus and arsenic pentoxides below a red heat, and iodic anhydride on gently heating. It also readily reduces lead and manganese peroxides, lead monoxide, and mercurous and mercuric chlorides. It is oxidised by fused potassium hydroxide, but is not attacked by fused potassium chlorate, and in this respect differs from



niobium. It is also less readily attacked than niobium by fused potassium nitrate. Tantalum is not attacked by single acids or by aqua regia, but like niobium and silicon it is oxidised by a mixture of aqua regia and hydrofluoric acid. In general chemical behaviour, tantalum resembles the non-metals rather than the metals. C. H. B.

**Platinum Tetraiodide.** By ITALO BELLUCCI (*Atti R. Accad. Lincei*, 1902, [v], 11, i, 8—12).—The author finds that, like the chloride and bromide, platinic iodide behaves as an anhydride and takes up 2 mols. of water to form an acid of the composition  $[\text{PtI}_4(\text{OH})_2]\text{H}_2$ . This is shown by allowing the iodide to remain for some time in contact with 95 per cent. alcohol, by which means a solution having an intense chestnut-brown colour is obtained. This liquid, which is decomposed by light, has an acid reaction and decomposes carbonates. When treated with concentrated aqueous solutions of salts of various metals, it yields precipitates which are found to be salts of an acid having the formula just given: The following salts, which are, in general, of a reddish-brown or chestnut colour, have been prepared:  $[\text{PtI}_4(\text{OH})_2]\text{Ag}_2$ ;  $[\text{PtI}_4(\text{OH})_2]\text{Pb,Pb}(\text{OH})_2$ ;  $[\text{PtI}_4(\text{OH})_2]\text{Ti}_2$ ; and  $[\text{PtI}_4(\text{OH})_2]\text{Hg}$ .  
T. H. P.

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## Mineralogical Chemistry.

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**Chalmersite, a New Sulphide of the Copper-glance Group.** By EUGEN HUSSAK (*Centr. Min.*, 1902, 69—72).—This mineral is found associated with copper-pyrites, pyrrhotite, calcite, siderite, dolomite, albite, quartz, &c., in the Morro Velho gold-mine, Minas Geraes, Brazil. The acicular crystals are very similar to copper-glance in habit, twinning and angles [ $a:b:c=0.5734:1:0.9649$ ]. The colour is bronze-yellow;  $H=3\frac{1}{2}$ ; sp. gr. 4.68. The mineral is magnetic like pyrrhotite. From the following analysis by Florence (on only 0.016 gram) the formula is given as  $Cu_2S, Fe_6S_7$ :

Fe.	Cu.	S.	Total.
46.95	17.04	35.30	99.29

The mineral is isomorphous with copper-glance, and its existence suggests that there may be a form of  $Fe_nS_{n+1}$  dimorphous with pyrrhotite. The fact that copper-glance has not been found at Morro Velho is considered to negative the suggestion that the new mineral may be only crystals of copper-glance partly replaced by pyrrhotite.

L. J. S.

**New Occurrence of Sperrylite.** By HORACE L. WELLS and SAMUEL L. PENFIELD (*Amer. J. Sci.*, 1902, [iv], 13, 95—96).—A specimen of platiniferous copper ore from the Rambler mine in the Medicine Bow Mountains, Wyoming, was found to consist of covellite enclosing a few minute cubic crystals of sperrylite ( $PtAs_2$ ).

L. J. S.

**Analysis of the Saccharoid Marble of Carrara.** By EGIDIO POLLACCI (*Gazzetta*, 1902, 32, i, 83—87).—This marble is white, with occasional bluish-black veins and blackish, linear dottings, and gives a saccharoidal fracture. Under the lens, it appears to be formed of crystals in which the rhombobedral form is visible. Its composition in parts per 1000 is: CaO, 553.8; MgO, 5.891; Fe<sub>2</sub>O<sub>3</sub> (maximum), 0.6834; Al<sub>2</sub>O<sub>3</sub>, 0.5024; Na<sub>2</sub>O, 0.1334; (NH<sub>4</sub>)<sub>2</sub>O, 0.1116; CO<sub>2</sub>, 436.96; P<sub>2</sub>O<sub>5</sub>, 0.965; Cl, 0.458; SO<sub>3</sub>, 0.18; N<sub>2</sub>O<sub>5</sub>, 0.0025; N<sub>2</sub>O<sub>3</sub>, 0.0004; SiO<sub>2</sub>, 0.01; organic matter, 0.079; difference, 0.2233. The author considers that the above analysis leaves no room for doubt as to the organic origin of the marble.

T. H. P.

**The Marbles of Assynt.** By J. J. HARRIS TEALL and WILLIAM POLLARD (*Summary of Progress, Geol. Survey United Kingdom* for 1900, 1901, 151—156).—The plutonic mass of Cnoc na Sròine in Sutherland, consisting mainly of red granite or syenite, shading off into typical nepheline-syenite and borolanite, is intrusive into Durness dolomites. The metamorphosed dolomites contain, in different portions, brucite, diopside, tremolite, mica, forsterite and serpentine. Brucite (anal. I, sp. gr. 2.41) occurs in fibrous or scaly aggregates, and is probably an alteration product after periclase; in association with calcite and dolomite, it forms a white rock practically identical with the predazzite of the Tyrol. Forsterite (anal. II and III) occurs as grains in a white rock, composed of this mineral and calcite; the serpentine (ophicalcite) has been derived by its alteration. Analysis IV is of forsterite from Skye. In other varieties of the altered rocks, tremolite is invariably associated with calcite, whilst diopside is frequently associated with dolomite, thus indicating that the rocks are altered siliceous dolomites, since the development of tremolite (CaO, 3MgO, 4SiO<sub>2</sub>) in dolomite would naturally be accompanied by the formation of calcite, whereas diopside (CaO, MgO, 2SiO<sub>2</sub>) could be formed directly by the simple substitution of silica for carbon dioxide.

In some cases, a green ægirine-augite (anal. V, also TiO<sub>2</sub>, Li<sub>2</sub>O, traces) occurs in the dolomite, indicating that there has been an intimate blending of sedimentary and igneous material accompanied by some interchange of constituents:

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Loss on igni- tion.	Total.
I.	0.4	1.4	—	—	—	0.8	66.0	—	—	31.2	99.8
II.	42.2	0.8	0.5	—	—	0.3	57.0	—	—	0.3	101.1
III.	42.6	1.2	1.2	—	—	0.6	51.2	—	—	3.1	99.9
IV.	41.5	0.9	1.4	—	—	0.3	55.6	—	—	1.2	100.9
V.	53.58	1.32	9.46	3.36	0.31	16.82	11.67	0.20	3.31	0.73	100.76

Analyses are also given of rocks, and of the felspars isolated from them, from the North-west Highlands.

L. J. S.

**Anapaite: a New Mineral.** By A. SACHS (*Sitzungsber. Akad. Wiss. Berlin*, 1902, 18—21).—This mineral was found on limonite in the iron mine Scheljesni Bog, near Anapa, on the Black Sea. It forms platy or radially crystallised masses, less often distinct, transparent crys-

tals, of a pale greenish colour and with a bright vitreous lustre. Results are given of the goniometric measurements and optical determinations made on the triclinic crystals. Analysis gave the following results, from which is deduced the formula  $\text{FeCa}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ . Water is expelled only at a high temperature, and it has an acid reaction :

FeO.	CaO.	P <sub>2</sub> O <sub>5</sub> .	H <sub>2</sub> O.	Alkal.	Total.	Sp. gr.
18·07	27·77	35·51	18·47	trace	99·82	2·81

The new mineral is closely related to, but considered to be distinct from, the triclinic messelite,  $(\text{Ca}, \text{Fe}, \text{Mg})_3(\text{PO}_4)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ , for which was approximately determined the angle  $am = 42-43^\circ$ , and the extinction on  $a$ , referred to the edge  $a/m$ ,  $= 20^\circ$ ; the corresponding values for anapaite are  $44^\circ 55'$  and  $15^\circ$ .  
L. J. S.

**Wavellite from Manziana (Province of Rome).** By FER-  
RUCCIO ZAMBONINI (*Atti R. Accad. Lincei*, 1902, [v], 11, i, 123—125).  
—The author describes a specimen of wavellite, occurring in spheres and hemispheres having a perfect, radiating, fibrous structure and a very pale greenish surface colour. Its composition is : P<sub>2</sub>O<sub>5</sub>, 33·76 ; Al<sub>2</sub>O<sub>3</sub>, 37·11 ; H<sub>2</sub>O, 26·69, and F, 2·05 per cent., which agrees well with that given by Groth.  
T. H. P.

**Action of Ammonium Chloride on certain Silicates.** By  
FRANK W. CLARKE and GEORGE STEIGER (*Amer. J. Sci.*, 1902, [iv], 13, 27—38. Compare Abstr., 1900, ii, 24, 219, 414).—In continuing their investigation of the action of ammonium chloride on silicates, the authors now give their results obtained with the following minerals. Stilbite from Wasson's Bluff, Nova Scotia (anal. I, fractional water under 1A); heulandite from Beruförd, Iceland (anal. II); chabazite from Wasson's Bluff, Nova Scotia (anal. III, fractional water IIIA); thomsonite from Table Mountain, Golden, Colorado (anal. IV, fractional water IVA); ilvaite from Golconda Mine, Owyhee Co., Idaho (anal. V, by Hillebrand; H<sub>2</sub>O at 105°, 0·15; above 105°, 2·64); ægirite from Magnet Cove, Arkansas (anal. VI; H<sub>2</sub>O at 100° 0·15; above 100°, 0·40). Also riebeckite (?), serpentine, leuchtenbergite, and phlogopite, of which analyses have already been published :

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.
I.	55·41	16·85	0·18	—	—	7·78
II.	57·10	16·82	—	—	—	6·95
III.	50·78	17·18	0·40	—	—	7·84
IV.	41·13	29·58	—	—	—	11·25
V.	29·16	0·52	20·40	29·14	5·15	13·02
VI.	50·45	2·76	23·42	5·26	0·10	5·92

	SrO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	—	0·05	—	1·23	19·01	100·51
II.	0·46	0·07	0·42	1·25	16·61	99·68
III.	—	0·04	0·73	1·28	21·85	100·10
IV.	—	—	—	5·31	13·13	100·40
V.	—	0·15	—	0·08	2·79	100·41
VI.	—	1·48	0·24	—	0·55	100·02

	H <sub>2</sub> O at 100°	180°	250°	350°	Low redness.	Full redness.	Blowpipe.	Total.
IA.	3·60	6·46	3·80	2·10	2·95	0·06	0·04	19·01
IIA.	3·62	13·00						16·61
IIIA.	5·22	5·70	3·92	2·36	4·51	0·13	0·01	21·85
IVA.	1·01	1·44	1·05	3·90	5·65	—	0·08	13·13

The zeolites, stilbite, &c., behave in much the same manner as previously described for other zeolites, natrolite, &c. (Abstr., 1900, ii, 414). When heated in a sealed tube with ammonium chloride at 350°, they are decomposed with the formation of ammonium derivatives, ammonium more or less completely replacing the calcium and sodium. From these zeolites, either before or after ignition, very little silica is extracted by sodium carbonate solution; they cannot therefore be represented as metasilicates. Stilbite, heulandite and chabazite approximate more or less nearly to trisilicates in their composition, whilst thomsonite is essentially an orthosilicate with variable admixtures of trisilicate molecules.

The other minerals examined do not yield ammonium derivatives when heated with ammonium chloride, but ilvaite is strongly attacked, riebeckite moderately, and the others only feebly.

L. J. S.

**Composition of Yttrialite and Thalenite.** By WILLIAM F. HILLEBRAND (*Amer. J. Sci.*, 1902, [iv], 13, 145—152).—The formula,  $R_2O_3 \cdot 2SiO_2$ , of yttrialite having recently been called into question, the mineral has been submitted to a new analysis, but with no very satisfactory result. The material analysed was purified with acid; the sp. gr. before being so treated was 4·59, and afterwards 4·65. The new results are:

SiO <sub>2</sub> .	TiO <sub>2</sub> .	ThO <sub>2</sub> .	UO <sub>2</sub> .	Ce <sub>2</sub> O <sub>3</sub> .	La <sub>2</sub> O <sub>3</sub> , &c.	Y <sub>2</sub> O <sub>3</sub> , &c.	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	
29·63	0·05	10·85	1·64	3·07	5·18	43·45	0·76	1·96	
MnO.	PbO.	CaO.	MgO.	H <sub>2</sub> O(>105°).	H <sub>2</sub> O(<105°).	CO <sub>2</sub> .	P <sub>2</sub> O <sub>5</sub>	F, Alkalis.	Total
0·88	0·80	0·67	0·16	0·32	0·04	0·11	0·12	traces	99·69

Between 1 and 2 c.c. of nitrogen (?) and helium (?) are present in a gram of yttrialite. These results, which agree fairly well with Mackintosh's analysis, lead to the formula  $R''_{61}R'''_{286}R''''_{47}(Si_2O_7)_{247}$ , or deducting the thorium and uranium as thorite,  $R''_{61}R'''_{286}Si_{447}O_{1533}$ : the latter, written as a basic salt of metasilicic acid, is approximately  $R''R'_{3}(R''O)_3(SiO_3)_7$ . Reasons are given for considering as doubtful the formula assigned to the recently described mineral thalenite (Abstr., 1899, ii, 766). Possibly the presence of helium and other gases in these minerals may have something to do with the difficulty in deducing satisfactory formulæ.

L. J. S.

**Mineral Water of Poleo, near Schio [Italy].** By PIETRO SPICA and GUIDO SCHIAVON (*Gazzetta*, 1902, 32, i, 63—74).—This water, when collected, was issuing at the rate of 1·16 litres per minute at a temperature of 13·9°, that of the air being 25°; its sp. gr. is 1·0012 at 25°/4°. A detailed analysis is given of the water, which may be classed as ferrugino-manganiferous.

T. H. P.

**Mineral Water from the Jolanda Spring, near Staro [Italy].**  
By PIETRO SPICA and GUIDO SCHIAVON (*Gazzetta*, 1902, **32**, i, 75—83).  
—This water much resembles that from the Royal Spring near Staro.  
A detailed analysis is given. T. H. P.

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## Physiological Chemistry.

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**Blood-Platelets.** By GEORGE T. KEMP and O. O. STANLEY (*Proc. Amer. Physiol. Soc.*, 1902; *Amer. J. Physiol.*, 6, xi).—Blood-platelets on agar-agar containing sodium hexametaphosphate, execute ameboid movements; this confirms an observation previously made by Dietjen (*Virchow's Archiv*, 1901, 164, 239). After intravenous injection of methylene-blue, the platelets contain blue-stained granules. The granules appear to be composed of nucleo-proteid. W. D. H.

**The Number of Blood-Platelets at High Altitudes.** By GEORGE T. KEMP (*Proc. Amer. Physiol. Soc.*, 1902; *Amer. J. Physiol.*, 6, xi—xii).—The red corpuscles and platelets were counted in Paris; the mean per cubic millimetre gave 4,800,000 and 457,000 respectively; the ratio of platelets to red corpuscles was thus 1:10.5. In forty-eight hours a journey was made to the Gorner Grat, 10,290 feet above sea level; the ascent was made by railway to exclude fatigue. Seventy-two hours after the last count in Paris, the numbers were 7,000,000 and 1,206,900, the ratio being 1:5.8. The size of the platelets had increased; the number of small red corpuscles was also large; no connecting form between the two could be discovered. W. D. H.

**Rôle of the Cell Nucleus in Oxidation and Synthesis.** By R. S. LILLIE (*Proc. Amer. Physiol. Soc.*, 1902; *Amer. J. Physiol.*, 6, xv—xvi).—Fresh and alcoholic tissues of the frog were treated with an alkaline solution of *p*-phenylenediamine and  $\alpha$ -naphthol. This turns violet on oxidation from the formation of indophenol. The coloration is most intense, and appears most readily in those regions where nuclei are most densely aggregated; for instance, in kidney, spleen, and thymus. The phenomenon is prevented by acids, by reducing substances, and by poisons like hydrocyanic acid, which interfere with oxidation. W. D. H.

**Occurrence of *p*-Hydroxyphenylethylamine in Pancreatic Digestion. Fermentative Origin of Carbon Dioxide.** By R. L. EMERSON (*Beitr. chem. Physiol. Path.*, 1902, 1, 501–508).—In addition to the numerous substances of small molecular weight which are known to result from the pancreatic digestion of proteids, there are several others, of which one only, *p*-hydroxyphenylethylamine, is described in the present paper; as it increases, the amount of tyrosine diminishes, hence it is formed from the latter by removal of the elements of carbon

dioxide. This fermentative formation of carbon dioxide without the taking up of oxygen or water is regarded as a point of interest.

W. D. H.

**The End Product of Peptic Digestion.** By LEO LANGSTEIN (*Beitr. chem. Physiol. Path.*, 1902, 1, 507—523).—Very prolonged gastric digestion leads to the formation of simple products similar to those produced in a shorter time by the pancreatic digestion of proteids. Among the substances identified were leucine, tyrosine, glutamic acid, and (probably) *p*-hydroxyphenylethylamine; the substances intermediate between peptone and amino-acids, described by Pfäundler were not discovered; possibly in these experiments digestion had gone too far.

W. D. H.

**Influence of Hydroxides of Barium, Calcium, and Strontium on Tryptic Digestion.** By ALBERT DIETZE (*Chem. Centr.*, 1902, i, 328—329; from *Inaug. Diss. Leipzig*, 1900).—The optimum of tryptic digestion was obtained if the digestive fluid contains barium hydroxide, 0.06 to 0.15, calcium hydroxide, 0.034 to 0.054, or strontium hydroxide, 0.058 to 0.085 per cent. These numbers correspond with a gram-mol. in from 114 to 285 litres. In the case of potassium carbonate, the optimum of digestion is obtained where a gram-mol. is dissolved in from 13 to 25 litres.

W. D. H.

**Metabolism in Horses.** By THEODOR PFEIFFER (*Landw. Versuchs-Stat.*, 1902, 56, 283—288).—A criticism of Zuntz and Hagemann's experiments and conclusions (*ibid.*, 1901, 55, 112; compare Pfeiffer, *Abstr.*, 1900, ii, 554).

N. H. J. M.

[Metabolism in Horses.] By NATHAN ZUNTZ and O. HAGEMANN (*Landw. Versuchs-Stat.*, 1902, 56, 289—292).—A reply to Pfeiffer (preceding abstract).

**Formation of Phenol and Indoxyl as Intermediate Metabolic Products and their Relationship to Glycuronic Acid Excretion.** By CARL LEWIN (*Beitr. chem. Physiol. Path.*, 1902, 1, 472—500).—In phloridzin diabetes there is an increase in the indoxyl and phenol excreted. This is not due to intestinal putrefaction, but the substances in question are intermediate metabolites. Accompanying this there is an increase in the amount of glycuronic acid, which is probably the result of the phenol and indoxyl produced, and the acid is excreted in combination with these aromatic substances.

W. D. H.

**Metabolism of Phosphorus, Calcium, and Magnesium in Herbivora.** By FERENCZ TANGL (*Pflüger's Archiv*, 1902, 89, 227—239).—Experiments on horses, the principal conclusions from which are that the amount of drinking water makes no difference either on the absorption or metabolism of calcium and magnesium; that the amount of phosphorus in the urine shows some parallelism to nitrogen, and rises when that in the food increases; that the amount of calcium and magnesium in the excreta depends on the amount in the food. There appears to be some retention of calcium, for foods poor in that element may be taken for some time without injurious effects.

W. D. H.



**Influence of Fat and Carbohydrate on Proteid Metabolism.** By T. W. TALLQVIST (*Arch. Hygiene*, 1902, 41, 177—189).—The experiments on the author's person confirm the statement, made previously by several observers, that carbohydrate has a greater 'proteid-sparing' action than fat. Within the limits of the diets employed, the changed proportion between fat and carbohydrate has, however, very little influence on the total nitrogenous exchange.

W. D. H.

**Synthesis of Proteid in the Animal Body.** By OTTO LOEWI (*Chem. Centr.*, 1902, i, 329; from *Centr. Physiol.*, 1902, 15, 590—591).—A small dog was kept in nitrogenous equilibrium by feeding it on starch and sugar, *plus* the products of a pancreatic digestion which had passed beyond the stage of the biuret reaction. This confirms Kutscher and Seemann's, and also Cohnheim's, observations that the body is capable of synthesising proteids from its simpler constituents.

W. D. H.

**Absorption of Fat.** By EDUARD PFLÜGER (*Pflüger's Archiv*, 1902, 89, 211—226).—Polemical against O. Loewi.

W. D. H.

**Formation of Iodised Fat in the Mammary Glands.** By F. JANTZEN (*Chem. Centr.*, 1902, i, 219; from *Centr. Physiol.*, 1901, 15, 506—511).—Winternitz and Caspari consider the appearance of iodised fat in the milk after it has been given in the food as a proof that the food fat passes unchanged into the milk fat. That this assumption is incorrect is shown by the present experiments, for iodised casein (incompletely free from fat, it is true) leads to the same result. Iodide of starch and alkali iodides have not this effect.

W. D. H.

**Formation of Sugar from Fat.** By OTTO LOEWI (*Chem. Centr.*, 1902, i, 220—221; from *Arch. exp. Path. Pharm.*, 1901, 47, 68—76).—If fat is given to dogs suffering from phloridzin diabetes, or to human beings with severe diabetes, the relation of sugar to nitrogen in the urine is often higher than was found by Minkowski and by Lusk in the animals studied by them. This is attributed to the proteid sparing action of the fat. This sparing action leads to a retention of the nitrogenous portion of the proteid molecule, whilst the part which gives rise to sugar is not retained.

W. D. H.

**Does Dextrose arise from Cellulose in Digestion?** By GRAHAM LUSK (*Proc. Amer. Physiol. Soc.*, 1902; *Amer. J. Physiol.*, 6, xiii).—In phloridzin diabetes, if dextrose is given, it is quantitatively eliminated in the urine. Since cellulose given in such a case does not increase the dextrose of the urine, it follows that dextrose is not produced from cellulose during digestion.

W. D. H.

**Physiological Importance of Pentosans.** By JOSEF KÖNIG and FR. REINHARDT (*Zeit. Nahr. Genussm.*, 1902, 5, 110—116).—After feeding on pentosans, the urine contains only traces of furfuroids.

They appear also to have a 'sparing' effect on metabolism, and are therefore regarded as valuable from the nutritive standpoint.

W. D. H.

**Utilisation of Sugars (Bihexoses) in the Organism.** By ALBERT CHARRIN and BROCARD (*Compt. rend.*, 1902, 134, 188—190. Compare this vol., ii, 216).—When different bihexoses are simultaneously ingested into omnivorous animals accustomed to an amylaceous diet, it is found that maltose is more readily hydrolysed than either lactose or sucrose. On comparing lactose and sucrose, it is found that lactosuria is less frequent than sucrosuria in animals having a milk diet, whilst the converse is true of animals consuming large quantities of sucrose. The facility with which these sugars are hydrolysed depends on the habitual diet; it is the alimentation which makes the ferment.

When very excessive doses of a bihexose are administered, the urine is found to contain this sugar and also the products of its hydrolysis.

G. T. M.

**Action of Alcohol as a 'Proteid-Sparer.'** By RUDOLF ROSEMAN (Pflüger's Archiv, 1902, 89, 178—210).—Polemical against R. O. Neumann (compare this vol., ii, 154).

W. D. H.

**Action of Alcohol on Muscle.** By FREDERIC S. LEE and WILLIAM SALANT (*Proc. Amer. Physiol. Soc.*, 1902; *Amer. J. Physiol.*, 6, xiii—xiv).—The experiments were made on frogs; the alcohol was given subcutaneously, and one gastrocnemius muscle was protected from the action of the drug and compared with the other. One to 4 minims of 10 per cent. alcohol per gram of frog increases muscular work by 10 per cent. Less than this has no effect; larger quantities are harmful.

W. D. H.

**Decomposition of Guanidine in the Animal Body.** By ERNST POMMERENIG (*Beitr. chem. Physiol. Path.*, 1902, 1, 561—566).—Guanidine is highly toxic. Doses smaller than poisonous ones are in rabbits excreted unchanged in the urine. Guanidine does not appear to be a normal oxidation product of arginine in the body.

W. D. H.

**Arsenic in the Animal Organism.** By KARL CERNY (*Zeit. physiol. Chem.*, 1902, 34, 408—416).—Like Hödlmoser (*Abstr.*, 1901, ii, 673), the author finds that Gautier's statement that arsenic is a normal and important constituent of various parts of the body is incorrect. Sometimes minimal traces are found which have no physiological significance.

W. D. H.

**Florence's Crystals.** By N. BOCARIUS (*Zeit. physiol. Chem.*, 1902, 34, 339—346).—The crystals first described by Florence as obtainable from spermatic fluid are now shown to be due to the presence of choline.

W. D. H.

**Amount of Iodine in Sheep's Thyroid.** By JAC. WOHLMUTH (*Chem. Centr.*, 1902, i, 327; from *Centr. Physiol.*, 15, 587—588).—Hungarian sheep, like those examined by Baumann, have in their

thyroids, iodothylin, which contains 3.2 to 3.3 per cent. of iodine. This is regarded as important, as the districts from which the sheep gathered food are far from the sea. W. D. H.

**Silicic Acid in the Tissues, especially in the Whartonian Jelly.** By HUGO SCHULZ (*Pflüger's Archiv*, 1902, 89, 112—118).—The amount of silicic acid is higher in the same tissues in youth than in old age. It is highest of all in the embryonic connective tissues, such as the Whartonian jelly. W. D. H.

**Relation between Spleen and Pancreas.** By LEO F. RETTGER (*Proc. Amer. Physiol. Soc.*, 1902; *Amer. J. Physiol.*, 6, xiv).—Spleen extracts, both *in vitro* and *in vivo*, increase the proteolytic power of pancreatic extracts. Other fluids intravenously injected (saline solution, boiled extracts of spleen, extracts of liver, pancreas, &c.) have no specific 'trypsinogenic' effects. W. D. H.

**The Mechanism of the so-called Peripheral Reflex Secretion of the Pancreas.** By WILLIAM M. BAYLISS and ERNEST H. STARLING (*Centr. Physiol.*, 1902, 15, 682—683).—The secretion which the pancreas pours out as the result of the application of acid to the intestinal wall occurs when all connections with the central nervous system are severed, and is therefore regarded as a reflex, having its centre in the ganglia of the solar plexus (Wertheimer and Lepage). It is now shown that it also occurs when all connections with the solar plexus are cut through. It must therefore be due to chemical stimulation of the pancreatic cells. The specific irritant is not the acid, as injection of 0.4 per cent. hydrochloric acid has no effect. It is something (a 'secretin') which is produced by the acid acting on some substance (prosecretin) in the mucous membrane of the duodenum and jejunum. If the mucous membrane is rubbed up with the acid, and the filtered product is injected, there is an immediate flow of the juice. The injection also produces a rise of blood-pressure. The substance which produces this effect is not the secretin, for extracts of the ileum similarly prepared have no action on the pancreatic secretion, but nevertheless produce a rise of blood-pressure.

The extract of jejunum produces its effect on secretion after the separation of all proteins. Secretin is soluble in alcohol or ether, and is probably a substance of small molecular weight. Further chemical examination of this material is in progress.

It is suggested that this observation may be the precursor of the discovery of other secretins in the body, and that Pawloff's work on the secretory action of the vagus nerve on the pancreas will need revision. W. D. H.

**Diuresis.** By JOHN T. HALSEY (*Proc. Amer. Physiol. Soc.*, 1902; *Amer. J. Physiol.*, 6, xvi—xvii).—Nussbaum's results on urinary secretion in frogs are confirmed. The tubular epithelium excretes urea and certain salts. Under the influence of theobromine or phloridzin, it has the power of excreting sugar also. W. D. H.

**Saline Diuresis.** By ARTHUR R. CUSHNY (*Proc. Amer. Physiol. Soc.*, 1902; *Amer. J. Physiol.*, 6, xvii—xviii).—Sodium sulphate given intravenously causes more profuse diuresis than does the chloride. Magnus and also Sollman consider this is because the sulphate stimulates the secretory elements of the kidney. A simpler explanation is given here on Ludwig's theory, namely, that the sulphate is not so readily absorbed by the renal tubules as the chloride, and so retains a larger amount of water.

W. D. H.

**Excretion of Phosphoric Acid in Flesh and Vegetable Feeders.** By W. BERGMANN (*Chem. Centr.*, 1902, i, 219—220; from *Arch. exp. Path. Pharm.*, 1901, 47, 77—81).—If dogs which usually excrete the excess of phosphoric acid in the food by the urine are given calcium also, the excess of the acid appears principally in the faeces. This is due to non-absorption, for if sodium phosphate is injected subcutaneously, the phosphoric acid is excreted by the kidneys whether calcium is given at the same time or not. In herbivora (sheep), subcutaneously injected phosphoric acid is completely excreted by the intestine. If glycerophosphoric acid is given hypodermically, it appears as inorganic phosphate in the urine of the dog but in the faeces of the sheep.

W. D. H.

**Excretion of Lithium.** By C. A. GOOD (*Proc. Amer. Physiol. Soc.*, 1902; *Amer. J. Physiol.*, 6, xx—xxi).—Lithium chloride was given to cats hypodermically; 0.5 gram is fatal in about a week. Considerable amounts are obtainable from the stomach, bowel, and saliva, but when small doses are given repeatedly more is excreted in the urine than by the alimentary tract.

W. D. H.

**Allantoin Excretion.** By LAFAYETTE B. MENDEL (*Proc. Amer. Physiol. Soc.*, 1902; *Amer. J. Physiol.*, 6, xiv—xv).—Finely minced thymus gland mixed with water was introduced *per rectum* into dogs. The absorption of purine compounds was demonstrated by a rise in the allantoin and uric acid of the urine. Vegetable nucleates and nucleic acid prepared from wheat resemble the nucleo-proteids from animal tissues in metabolism, giving rise, in cats fed on them, to allantoin in the urine.

W. D. H.

**A Crystalline Urinary Albumose.** By ALIDE GRUTTERINK and CORNELIA J. DE GRAAFF (*Zeit. physiol. Chem.*, 1902, 34, 393—407).—A case of albumosuria is described; the proteid in question, as in so many of these cases, does not appear to be identical with any known albumose. By a modification of the ammonium sulphate method, it was obtained in a crystalline form, but other salts may also be employed.

W. D. H.

**Chemical Composition of Biliary Calculi.** By ANGILO FUNARO (*L'Orosi*, 1901, 24, 361—364).—The author gives the following analyses of two samples of biliary calculi removed from women subjected to cholecystotomy.

Cholesterol (and a little fatty matter), 90.87 and 90.08; water (at

100°), 4.60 and 4.50; bilirubin (chloroform extract), 0.81 and 0.19; biliverdin (alcoholic extract), 2.24 and 1.58; mineral matter, 0.88 and 2.72; soluble organic matter (gum, &c.), 0.14 and 1.53. Totals (1) 99.54 and (2) 100.60. The percentages of soluble mineral matter in the two cases were 0.71 and 0.45 and the total phosphoric acid, 0.203 and 0.997. T. H. P.

**Phloridzin Diabetes.** By OTTO LOEWI (*Chem. Centr.*, 1902, i, 363—364; from *Arch. exp. Path. Pharm.*, 1901, 47, 48—55; 56—67).—The glycosuria produced by feeding on phloridzin is less intense than that caused by hypodermic or intravenous injection of that drug; this is simply because phloridzin is not wholly absorbed in the alimentary canal, but part passes out with the faeces.

The simultaneous administration of camphor and phloridzin causes the amount of sugar in the urine to be slightly lessened; this will not account for the large amount of camphor-glycuronic acid which appears. Probably, therefore, the source of the sugar and the glycuronic acid in the body is different. W. D. H.

**Proteid Metabolism in Fever.** By S. WEBER (*Chem. Centr.*, 1902, i, 219; from *Arch. exp. Path. Pharm.*, 1901, 47, 19—47).—Sheep were infected with a febrile disease, and at the same time given abundant nourishment; in the first experiment, the daily intake of nitrogen was 1.36 grams, and the output 1.1 grams. In the second experiment, the numbers were 7.8 and 4.7 respectively; in the latter case, lactose was added to the food. It is thus possible to obtain a putting on of proteid even during fever. W. D. H.

**Metabolism in a Case of Lymphatic Leucæmia.** By YANDELL HENDERSON and C. H. EDWARDS (*Proc. Amer. Physiol. Soc.*, 1902; *Amer. J. Physiol.*, 6, xxii).—The uric acid and phosphates were found rather below than above the normal. It therefore appears, as Milroy and Malcolm stated, that the nuclein metabolism of leucæmia differs from that produced by injecting nuclein, and depends, not on an increased formation of leucocytes, but on their diminished katabolism. W. D. H.

**Leucocytosis following Intravenous Injections of Sodium Cinnamate.** By H. BATTY SHAW (*J. Path. Bact.*, 1902, 8, 70—81).—Richter and Spiro's observations on the general leucocytosis produced by sodium cinnamate are confirmed; the present experiments were made on cats. The effect is not produced by a loss of water in the blood. The simpler lymphocytes are stimulated to transformation into polymorpho-nuclear and intermediate forms. The spleen does not appear to aid or hinder the change. Eosinophile cells are diminished. Ether has a similar, although not so marked, effect. W. D. H.

**Toxic and Antitoxic Action in Vitro and in Corpore.** By ERNEST F. BASHFORD (*J. Path. Bact.*, 1902, 8, 52—69).—Differences between the interaction of toxins and antitoxins as it occurs in the body and outside of it are pointed out. It is suggested

that the action *in vitro* should be termed pseudoantitoxic, as the poison is there incapable of leading to the production of an antitoxin.

W. D. H.

**The Poison of the Daboia Russellii.** By GEORGE LAMB and WILLIAM HANNA (*J. Path. Bact.*, 1902, 8, 1—33).—Daboia venom owes its toxicity mainly, if not entirely, to its action on the blood. It causes rapid death from intravascular clotting, whilst in chronic cases there is a marked deficiency of blood coagulability, to which condition hæmorrhages, which are frequent, are probably due. The poison loses its activity by heating it to 73° for 3 hours, if a weak solution (0.1 per cent.) is used; the toxicity is lessened, but not destroyed, by such treatment if a strong (1 per cent.) solution is employed.

Daboia venom contains no substance comparable to the tox-albumose of cobra venom, and the latter contains no substance which causes intravascular coagulation. Calmette's serum has no power to neutralise the toxin of daboia venom.

W. D. H.

**Toxicology of Selenium and its Compounds.** By I. O. WOODRUFF and WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1902, *Amer. J. Physiol.*, 6, xxix—xxx).—Selenium is much more toxic than tellurium, although its poisonous effects are qualitatively much the same, and further resemble those produced by arsenic.

Four mg. of a selenite or selenate per kilo. of body weight in dogs kills in a few minutes. The element itself, when given by the mouth, is discharged *per rectum* and does no harm. The introduction of soluble salts is quickly followed by elimination in breath and urine. The distribution of selenium between the organs is similar to that of tellurium.

W. D. H.

**The Poison of Toads.** By FR. PRÖSCHER (*Beitr. chem. Physiol. Path.*, 1902, 1, 575—582).—The poisonous secretion of the toad's skin is present also to some extent in the blood. It is termed *phrynosysin*. It possesses hæmolytic properties, especially on sheep's blood, but has no such action on toad's blood. Other animals are intermediate between these two extremes. Like other lysins, it appears to consist of two substances. Normal rabbits' serum contains no antitoxin to this material, but one appears during the process of immunisation produced in the usual way.

W. D. H.

**Zygadenus Venenosus (Poison Camass).** By REID HUNT (*Proc. Amer. Physiol. Soc.*, 1902; *Amer. J. Physiol.*, 6, xix—xx).—Both the chemical and physiological properties of the active principle of *Zygadenus venenosus* agree very closely with those of veratrine. It is excreted rapidly in the urine, and is absorbed rather slowly from the stomach. By diuretics, it may be removed from the circulation so rapidly that few poisonous symptoms result.

W. D. H.

**Immune Substances.** By ERNST P. PICK (*Beitr. chem. Physiol. Path.*, 1902, 1, 445—471).—A further attempt, in the main unsuccessful, to identify the immune substances with various proteids of the

serum. The experiments chiefly relate to the coagulins of anti-typhoid serum, and are principally concerned with the action of various reagents (acids, alkalis, digestive ferments, &c.) on the coagulin and agglutinin; the principal conclusion arrived at is that agencies which affect, even in a slight degree, the properties of the proteids, lessen or annul the characteristic properties of the substances in question.

W. D. H.

**Putrefaction of Corpses.** By LUDWIG SCHMELCK (*Chem. Zeit.*, 1902, 26, 11).—An analysis of water found in an exhumed coffin which had been buried for about 50 years. Of the body there only remained the skeleton and some *débris* of clothing. The result was as follows: Residue, 0.404; after ignition, 0.303; calcium sulphate, 0.209; calcium phosphate, 0.024; calcium carbonate, 0.023; sodium chloride, 0.027 gram per litre. Oxygen consumed (Kubel's process), 0.0043 gram per litre, and ammonia and nitric acid undetectable. No odour was noticed on removing the lid. The bacteriological investigation has not been concluded.

L. DE K.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Composition of the Proteids and Cell-membranes in Bacteria and Fungi.** By K. S. IWANOFF (*Beitr. chem. Physiol. Path.*, 1902, 1, 524—537).—The proteids and cell-membranes were separated by Krawkoff's method. The proteids are nucleo-proteids, containing in bacteria nitrogen 16·3, and phosphorus from 1·8 to 2·2 per cent. In fungi, the percentage of nitrogen in the nucleo-proteid is 15·1 to 16·2, and of phosphorus 0·7 to 1. This accords with recent microscopic observations which have shown the presence of nuclear material in these cells. The existence in the cell-membranes of chitin apparently identical with animal chitin is confirmed. W. D. H.

**Bacteria which Hydrolyse Albumin.** By OSKAR EMMERLING and O. REISER (*Ber.*, 1902, 35, 700—702).—The exact action of *Bacillus fluorescens liquefaciens* on proteid substances is not yet known with certainty; the microbe may be one of the putrefaction bacteria, or it may contain an enzyme related either to pepsin or trypsin. The organism rapidly attacks ordinary gelatin in 10 per cent. solution, particularly at the surface of the liquid, and in order to facilitate the hydrolysis the mixture is often stirred. After several months, the liquid has a strong ammoniacal odour, about 25 per cent. of the nitrogen in the gelatin having been eliminated as ammonia. In spite of the prolonged interaction, the solution contains an appreciable amount of peptones, gases are not evolved, and phenols, indole, skatole, hydrogen sulphide, and diamines, the characteristic products of putrefaction, are not present. Methylamine, trimethylamine, choline, and betaine were,



however, identified in the solution; this result indicating that the bacillus is neither a putrefactive bacterium nor a producer of poisonous ptomaines; it appears to peptonise the proteids, and then slowly de-grade the products of hydrolysis to simple monoamines.

The proteolytic action of the bacillus on blood fibrin suspended in water containing toluene is very slow, and the mixture contains a considerable amount of peptone, even after prolonged treatment; arginine, leucine, and aspartic acid were distinguished in the product, this result indicating that the bacillus contains an enzyme resembling trypsin. The action, however, is very slow and incomplete, and resembles that induced by papayotin.

Sucrose, maltose, lactose, amygdalin, and  $\alpha$ - and  $\beta$ -methylglucoside are not attacked by *Bacillus fluorescens*; malic acid is converted into fumaric acid, and carbamide is slowly hydrolysed, but the ammonia liberated kills the organism. A sugar reducing Fehling's solution and forming phenylglucosazone is obtained from old cultures of the bacillus in malt infusions; starch and trehalose are slowly hydrolysed by the microbe.

G. T. M.

**Immunisation against Immune Serum.** By E. W. AINLEY WALKER (*J. Path. Bact.*, 1902, 8, 34—51).—A bacterium may be immunised against its immune serum, and thereby becomes more virulent and less agglutinable, if it is of an agglutinable variety. The immune serum in which its own bacillus has been grown is rendered less agglutinative and less protective against that bacillus. Agglutinins are true anti-substances. The basis of bacterial virulence and of chemiotactic influence is identical, and constitutes that group which causes the production of the immune substance. An animal may be immunised against an immune serum; it is then less capable of being protected by that serum, but its susceptibility to the attack of the bacterium is not increased. The immune substance is not identical in different animals for the same bacterium, but exhibits a specialism to the species.

W. D. H.

**Osmotic Exchanges.** By ALEXANDER NATHANSOHN (*Chem. Centr.*, 1902, i, 325—326; from *Ber. deutsch. botan. Ges.*, 19, 509—513).—Experiments with solutions of salts and non-electrolytes on the osmotic exchanges through the membranous walls of certain marine algæ.

W. D. H.

**Nitrogen Supply and Proteid Formation in Plants.** By FRIEDRICH CZAPEK (*Beitr. chem. Physiol. Path.*, 1902, 1, 538—560).—The gist of the paper is the importance of amino-compounds in the synthesis of proteids in plants.

W. D. H.

**Can Leucine and Tyrosine serve as Nutrients for Plants?** By ERNST SCHULZE (*Landw. Versuchs-Stat.*, 1902, 56, 293—296. Compare this vol., ii, 165).—After referring to Overton's statement (*Vierteljahresschr. Naturforsch. Ges. Zürich*, 1899, 44) that amino-acids belong to those substances which hardly appreciably enter into the living protoplasm, the author quotes some of his earlier results,

which seem to exclude the possibility of the leucine having been assimilated after decomposition (*Zeit. physiol. Chem.*, 1886, 10, 134, and 1892, 17, 513).

Glutamic acid (inactive) is assimilated by *Penicillium glaucum*. The residue recovered from the solution was found to be optically active. N. H. J. M.

**Changes in Nitrogenous Substances during the Ripening of some Cereals.** By N. K. NEDOKUTSCHAEFF (*Landw. Versuchs-Stat.*, 1902, 56, 303—310).—Determinations of dry matter, and of total nitrogen, and nitrogen in the forms of proteids, asparagine, and amides, were made in the grain of rye, wheat, barley, and oats at six different periods. It was found that whilst the percentage of proteid nitrogen increases as ripening proceeds, the nitrogen in other forms, especially asparagine, diminishes. The percentage of total nitrogen diminishes in wheat and rye, but increases in oats and barley. N. H. J. M.

**Ripening of Apples.** By RICHARD OTTO (*Bied. Centr.*, 1902, 31, 107—108; from *Proskau. Obstbau-Zeit.*, 1901).—Analyses were made of apples taken from the trees at intervals of fourteen days and of similar apples after being stored.

The percentage of water increased during ripening. The starch diminished from 3.99 (Sept. 7) to 1.60 (Oct. 5), and disappeared altogether when the apples were stored; the ash in the dry matter decreased, whilst the cellulose remained constant. As regards nitrogen, there was an increase during ripening on the trees, but afterwards a decrease.

The sp. gr. of the must, and the amounts of total sugar and glucose increased. The sucrose in the must increased during the ripening of the apples, but diminished in the case of stored apples. The acidity diminished both before and after the apples were taken off the trees. The amount of non-sugar reducing Fehling's solution in the must is small, and decreases during ripening. N. H. J. M.

**Examination of Asparagus Seeds.** By W. PETERS (*Arch. Pharm.*, 1902, 240, 53—56).—Seeds of *Asparagus officinalis* were found to contain water 11.5, woody fibre 8.2, nitrogen 3.0, and oil 15.3 per cent. Starch was not found, but there was *reserve-cellulose* (mannan); this was converted by boiling with 6 per cent. hydrochloric acid into *d*-mannose (seminose, Reiss, Abstr., 1889, 687), which was isolated and identified in the form of its phenylhydrazone; the seeds yielded 37.5 per cent. of mannose.

The oil was reddish-yellow in colour, and is a drying oil. It had sp. gr. 0.928 at 15°, and the refractometer indication in the Zeiss refractometer was 75 (1.75) at 25°. The saponification number was 194.1; the iodine number, with eighteen hours' digestion, 137.1; the acetyl-acid number, 179.2; the acetyl-saponification number, 204.4. The oil was found to consist of the glycerides of palmitic, stearic, oleic, linolic, linolenic and isolinolenic acids; these were liberated by hydrolysing the oil with potash, and the last four were identified by the products they yielded on oxidation with alkaline permanganate,

namely, dihydroxystearic, tetrahydroxystearic (sativic), linusic, and *isolinusic* acids respectively.

C. F. B.

**The Fatty Oil of Semen Coccognidii.** By W. PETERS (*Arch. Pharm.*, 1902, 240, 56).—The seeds contain 36—37 per cent. of a drying oil, with sp. gr. 0.924 at 15°, saponification number 196—197, iodine number (after eighteen hours' digestion) 125.9—126.3, acetyl-acid number 191.5, acetyl-saponification number 209.1. Palmitic, stearic, oleic, linolic, linolenic, and *isolinolenic* acids were obtained from it.

C. F. B.

**Carbohydrates Present in the Seed of Phellandrum Aquaticum.** By CHAMPENOIS (*J. Pharm. Chim.*, 1902, [vi], 15, 228—233. Compare Abstr., 1900, ii, 301).—The fruit of *Phellandrum aquaticum* contains 0.426 per cent. of sucrose. Arabinose and galactose were identified as the chief products of the partial hydrolysis of the fruit. The insoluble residue from this hydrolysis was submitted to the Braconnot-Flechsig method of hydrolysis, when mannose and pentoses were found amongst the products of such action.

H. R. LE S.

**Chemistry of Solanum Chenopodium.** By C. EDWARD SAGE (*Pharm. J.*, 1902, [iv], 14, 174).—The leaves and fruits of *Solanum chenopodium* contain 0.15 per cent. and the stalks 0.07 per cent. of total alkaloid; the purified alkaloid gives the reactions of solanine.

E. G.

**Phytochemical Examination of Verbascum Sinuatum** (used to poison Fish) and some other Scrophulariaceæ. By L. ROSENTHALER (*Arch. Pharm.*, 1902, 240, 57—69).—The half-ripe fruits were freed from fat and chlorophyll by treatment with ether, extracted with boiling water, the extract mixed with magnesium oxide and evaporated to dryness, the powdered residue extracted with alcohol, and the alcoholic extraction precipitated fractionally with ether. A substance was thus obtained with the properties of a saponin, but peculiar in that it is soluble in cold absolute alcohol and its solution gives no precipitate with saturated aqueous barium hydroxide or with lead acetate solution.

*Verbascum-saponin* is a white, amorphous powder, optically inactive, and having the composition  $C_{17}H_{26}O_{10}$ , probably  $C_{68}H_{84}O_{20}(OH)_{20}$ . When heated with acetic anhydride and sodium acetate, it forms an amorphous *acetyl* derivative,  $C_{68}H_{84}O_{20}(OAc)_{20}$ . When heated at 150° with benzoic anhydride and sodium benzoate, it forms a somewhat crystalline *benzoyl* derivative,  $C_{68}H_{84}O_{20}(OH)_8(OBz)_{12}$ . It can be hydrolysed by boiling with 8 per cent. hydrochloric acid, when *verbascum-sapogenin* is precipitated and dextrose remains in solution; the two together correspond with only 94 per cent. of the saponin, however. The sapogenin can be crystallised from alcohol, and has the composition  $C_5H_8O$ ; the glucose was identified by means of its phenyllosazone.

No alkaloid could be detected in the fruits of *Verbascum sinuatum* or *V. phlomoides* (including *V. thapsiforme*), or in the seeds of *V. nigrum* or *V. Thapsus*. Saponin could not be detected in the fruits of *Paulownia*

*imperialis*, *Gratiola officinalis*, *Antirrhinum majus* or in the official *Flor. Verbascum*. In the fruits of *Verbascum phlomoides* (incl. *thapsiforme*), a substance with some of the properties of a saponin was obtained.

It was discovered incidentally that some organic substances are precipitated along with lead sulphide, and cannot be extracted from the precipitate with alcohol, but are set free when the sulphide is just oxidised to sulphate by the addition of hydrogen peroxide. This may be useful in separating such substances from mixtures. C. F. B.

**Is the Form of Cereal Plants influenced by Nitrogenous Manures?** By H. CLAUSEN (*J. Landw.*, 1902, 49, 365—388).—Nitrogenous manures tend to increase the length of the lower portions of the stems of cereals, whilst the upper portions are relatively shortened. Nitrates have far more effect than ammonium salts. The lengthening of the lower parts of the stems renders them weaker and less able to stand. Although ammonium salts produce more grain than nitrates, the crop is less liable to be laid than when nitrates are employed. N. H. J. M.

**Cultivation of Lucerne on Soils without Calcium Carbonate.** By PIERRE P. DEHÉRAIN and EM. DEMOUSSY (*Compt. rend.*, 1902, 134, 75—80. Compare this vol., ii, 167).—Lucerne was sown in 1900 on heath soil, containing much organic matter, and in 1901 on a soil from Brittany derived from gneiss. Both soils were free from calcium carbonate.

The heath soil contained a limited number of nodule-bacteria and produced comparatively few nodules on the roots of the plants. The nodules were mostly branched. Addition of calcium carbonate (10 per cent.) greatly increased the production of nodules and more than doubled the yield of lucerne. Garden soil alone (10 per cent.) had a very much greater effect than calcium carbonate and its addition to the soil resulted in the production of single nodules. Simultaneous addition of garden soil and calcium carbonate slightly increased the yield as compared with garden soil alone.

The soil derived from gneiss also contained bacteria which produce root nodules. Unlike clover (*loc. cit.*), lucerne grown on this soil was very little benefited by addition of calcium carbonate. Garden soil, however, doubled the yield of lucerne. The effect of inoculation with garden soil on the form of the nodules was very marked. The original soil bacteria produced mainly branched nodules, whilst under the influence of the garden soil bacteria the majority of nodules were single. Calcium carbonate, both alone and with garden soil, slightly increased the number of single nodules. N. H. J. M.

**Production of Arrowroot.** By E. LEUSCHER (*Zeit. öffentl. Chem.*, 1902, 8, 23—25).—The cultivation of *Maranta* and the preparation of arrowroot are described. The average percentage composition of the roots grown in Jamaica was found to be as follows :

Water.	Starch.	Dextrin and sugar.	Crude fibre.	Ether. extract.	Proteid.	Ash.
63·42	27·84	2·08	3·94	0·19	1·64	0·89

The ash consists chiefly of phosphoric acid and potassium carbonate. The pulped root, when steam distilled, yields a volatile oil.

N. H. J. M.

**Cassava.** By E. LEUSCHER (*Zeit. öffentl. Chem.*, 1902, 8, 10—11).—The yield of cassava roots on well irrigated land may be more than 32,000 lbs. per acre. The percentage composition of the roots (mean of six analyses) is as follows :

Water.	Starch.	Nitrogenous matter.	Crude fibre.	Sugar.	Ether extract.	Ash.
70.25	21.44	1.12	1.11	5.13	0.41	0.54

N. H. J. M.

**Sand Culture Experiments with Kohlrabi on the Manures which influence the Production of Heads.** By RICHARD OTTO (*Bied. Centr.*, 1902, 31, 99—100; from *Bot. Centr.*, 1901, 86, 33).—All the pots received, per 1 kilo. of sand, potassium nitrate (1 gram), sodium chloride (0.5 gram), calcium sulphate (0.5 gram), magnesium sulphate (0.5 gram), tricalcium phosphate (0.5 gram), and ferric hydroxide (0.2 gram). The pots of series 2, 3, 4, and 5 had, in addition : (2 and 3), 5.65 and 11.3 grams of potassium chloride ; (4 and 5), 5.65 and 11.3 grams of disodium hydrogen phosphate. The best results were obtained in series 1, the amounts of extra manures of the other series being excessive. Very little growth was obtained in series 4 and 5.

N. H. J. M.

**Phosphoric Acid in Wines.** By G. PATUREL (*Ann. agron.*, 1902, 28, 5—30).—Vines remove comparatively small amounts of phosphoric acid from the soil, and the greater portion of it is returned with the leaves and marc, &c. The phosphoric acid in wine amounts to about 3 kilos. per hectare.

Phosphatic manuring is, however, of importance both as regards the maturation and the quantity of the grapes, and it enables the grapes to resist cryptogamic diseases.

Muntz's observations that a relation exists between the value of wines and the amount of phosphoric acid they contain is confirmed. Most of the phosphoric acid of red wines is derived from the juice, and very little from the solid portions of the grapes ; these lose, however, an appreciable amount of phosphoric acid during fermentation.

N. H. J. M.

**Nitrogenous Manuring of Vines.** By PAUL WAGNER (*Bied. Centr.*, 1902, 31, 87—88; from *Hess. landw. Zeits.*, 1901, 382).—When 600 cwt. of dung is applied every three years, it is proposed that sodium nitrate should be applied each year, the total amounts of nitrate (in two applications) increasing from 400 kilos. the first year to 600 kilos. the third year. Instead of sodium nitrate (first application of 200 to 400 kilos.), ammonium sulphate (150—300 kilos.) may be used.

When no dung is employed, 700 kilos. of sodium nitrate are applied ;

400 kilos. (or 300 kilos. of ammonium sulphate) for the first and 300 kilos. for the second dressing.  
N. H. J. M.

**Molasses Foods.** By C. V. GAROLA (*Ann. agron.*, 1902, 28, 111—112; from *J. d'agric. prat.*, 1901, ii, 406).—Peat molasses containing 24 per cent. of peat and 76 per cent. of molasses had the following composition: water, 19.00; sugar, 31.70; soluble matters, 20.93; insoluble, 19.46; and ash, 8.91 per cent. Good results were obtained by feeding horses with the food.

A suitable food was prepared by mixing molasses (45 parts), sesame cake (27.5 parts), and ground earth-nut husks (27.5 parts).

N. H. J. M.

**Dried Brandy Residues.** By KARL DIETRICH (*Landw. Versuchs-Stat.*, 1892, 56, 321—366).—Results of analyses of grains, potatoes, the residuary liquors, and the dried residues by various investigators.

N. H. J. M.

**New Problems in Soil Inoculation.** By JULIUS STOKLASA (*Bied. Centr.*, 1902, 31, 76—80; from *Zeit. Landw. Versuchs-wes. Oesterr.*, 1900, 10).—The results of experiments in which bone-meal, with nutritive solutions, was inoculated with various microbes (*Bacillus megatherium*, *B. fluoresc. liq.*; *B. proteus vulg.*; *B. butyricus* Huppe; *B. mycoides*, and *B. mesentericus vulgatus*) showed in every case a very considerable production of amides as well as an increase in the soluble phosphoric acid.

In the next series of experiments, oats were grown in soil (not sterilised) manured with bone-meal, without inoculation, and inoculated with the same microbes. Inoculation was in every case beneficial, but the greatest yields of oats were obtained under the influence of *Bacillus megatherium* (or alinit) in presence of xylose. The results of the pot experiments were all in accordance with those of the bone-meal inoculation experiments. The least satisfactory results were obtained with *B. fluorescens liquefaciens*.

N. H. J. M.

**Soils suitable for Chestnuts.** By L. PICCIOLI (*Bied. Centr.*, 1902, 31, 75—76; from *Staz. Sper. Agrar. Ital.*, 1901, 745).—From the examination of the soils and subsoils of Italian chestnut forests, the conclusion was drawn that chestnuts require a moderate amount of lime, but that as much as 8 per cent. of lime is very injurious. Application of potassium neutralises to some extent the injurious action of lime.

It is not usual to manure chestnut forests. The author recommends manuring with superphosphate (3 cwt.), gypsum (2 cwt.), ammonium sulphate (1 cwt.), and potassium sulphate (1—5 cwt. per hectare).

The most suitable soils are those derived from trachyte, leucite, or basalt, and those from granite, syenite, and porphyry containing a little clay.

N. H. J. M.

**Nitrogen of Humus.** By A. DOJARENKO (*Landw. Versuchs-Stat.*, 1902, 56, 311—320).—The total nitrogen and the nitrogen in the form of amides, ammonia, and amino-acids was determined in humic acid from

five black soils (1—5), from a sandy black soil (6), and from a loamy black soil (7). The percentage amounts of nitrogen in the dried substance were found to be as follows :

		Nitrogen per cent. in the dried substance.			
		Total.	As amino-acids.	As amides.	As ammonium.
1.	Black soil (Nischni) .....	2.74	1.34	0.31	0.04
2.	„ (Tula) .....	3.38	1.81	0.41	0.08
3.	„ (Samara) .....	2.64	1.30	0.29	0.02
4.	„ „ .....	3.33	2.34	0.32	0.03
5.	„ (Tula) .....	4.59	1.01	0.48	0.06
6.	Sandy black soil (Poltawa) .....	3.65	1.26	0.27	0.07
7.	Loamy „ „ (Charkow) .....	4.02	1.96	0.22	0.03

N. H. J. M.

**Mineral in Jamaica Soils.** By E. LEUSCHER (*Zeit. öffentl. Chem.*, 1902, 8, 28—29).—The clay soils and subsoils of Jamaica were found to contain numerous black balls, 2 to 12 mm. in diameter, of the following percentage composition :

Water	Lost at 105°.	105—180°.	CaO.	MgO.	BaO.	MnO <sub>2</sub> .	Mn <sub>2</sub> O <sub>3</sub> .	Fe <sub>3</sub> O <sub>4</sub> :
15.50	7.55		0.52	0.29	1.15	20.02	2.71	19.09
			Al <sub>2</sub> O <sub>3</sub> .	Ni <sub>2</sub> O <sub>3</sub> .	CuO.	P <sub>2</sub> O <sub>5</sub> .	S.	Insoluble.
			7.22	0.40	0.14	0.55	trace	24.86.

The mineral contains, therefore, 14.75 per cent. of manganese and 13.6 per cent. of iron.

The amount of the mineral decreases with the depth, and only isolated balls occur below 2 metres. The soil produces good tobacco, and bananas and beans grow luxuriantly on it.

N. H. J. M.

**Green Manuring.** By OTTO PITSCH (*Ann. agron.*, 1902, 28, 59—61; from *J. d'agric. prat.*, 1901, i, 753 and 756).—The object of the experiment was to ascertain the amounts of total crop and nitrogen yielded by different leguminous plants. It was found that vetches and peas gave greater yields than blue lupins, but that the latter have the advantage that their roots penetrate the soil to a greater depth and thus prepare the subsoil for subsequent crops.

N. H. J. M.

### Analytical Chemistry.

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Modification of Hempel's Gas Analysis Apparatus. By THEODORE W. RICHARDS (*Zeit. anorg. Chem.*, 1902, **29**, 359—364. Also *Proc. Amer. Acad.*, 1901, **37**, 201).—The absorption pipette consists of a bulb of about 75 c.c. capacity provided with a narrow stem turned upwards at the bottom and fitted into a bottle containing an absorbing



liquid. The capacity of the bottle should be about double as great as that of the bulb.

The author uses a small burette (50 c.c.) for measuring the volume of the gas, the temperature being kept constant by means of a water-jacket. J. McC.

**Electrolytic Estimation of Iodine in Presence of Bromine and Chlorine.** By ERICH MÜLLER (*Ber.*, 1902, 35, 950—954).—When an alkaline or neutral solution containing various haloid salts is electrolysed, the iodide is quantitatively converted into iodate, which can be estimated by treatment with potassium iodide and titration with thiosulphate. To prevent the reconversion of iodate into iodide, the electrolysis is carried out in the presence of a little potassium chromate, which must be allowed for when titrating. The cathode used was a gauze of platinum wire, 10 cm. long and 0.5 mm. thick, the anode a piece of platinum foil 14 cm. square and platinised on each side; a current of 1 ampere for 1½ minutes is employed, and the *E.M.F.* must not exceed 1.7 volts or some bromide will be converted into hypobromite. R. H. P.

**Estimation of Hydrofluoric Acid in Aqueous Solutions.** By F. WINTELER (*Zeit. angew. Chem.*, 1902, 15, 33—34).—An improved table showing the relation between the specific gravity at 20° and the strength of hydrofluoric acid.

The table has been constructed by carefully taking the sp. gr. with a platinum hydrometer, and, with the usual precautions, titrating a definite amount of the acid with normal alkali free from carbon dioxide, using phenolphthalein as indicator. Litmus or methyl-orange cannot be employed. L. DE K.

**Analysis of Pyrites and Estimation of Sulphuric Acid.** By GEORG LUNGE (*Zeit. angew. Chem.*, 1902, 15, 73—74).—A reply to Auzenat (this vol., ii, 104). The addition of sodium chloride is superfluous, and there is also no necessity for heating above 100°. The barium sulphate has completely deposited after half-an-hour. Fresh experiments are given in support of this view. L. DE K.

**Precipitation of Sulphuric Acid in Native Potassium Salts.** By ZÖPFCHEN (*Chem. Zeit.*, 1902, 26, 159).—Before proceeding to the estimation of potassium by means of platinic chloride, it is necessary to remove sulphates by addition of barium chloride, any excess of which should be again removed by adding sulphuric acid; as, however, a trace of the latter does not interfere with the estimation, much time may be saved by merely adding barium chloride until precipitation has nearly ceased. L. DE K.

**Reaction of the Phenolsulphonic Reagent in the Determination of Nitrates by Grandval and Lajoux's Colorimetric Method.** By CARLO MONTANARI (*Gazzetta*, 1902, 32, i, 87—96).—The yellow coloration obtained in this test (*Abstr.*, 1885, 1093) has generally been supposed to be due to the formation of picric acid, but

the author shows that the first product of the reaction is probably *o*-nitrophenol, and this, in the presence of nitrates (which yield nitric acid), passes readily into 2 : 4- and 2 : 6-dinitrophenol. T. H. P.

**The Supposed Reaction of Brucine with Nitrous Acid.** By GEORG LUNGE (*Zeit. angew. Chem.*, 1902, 15, 1—3).—The statement made by Winkler (*Abstr.*, 1901, ii, 627); that brucine reacts with nitrous acid as well as with nitric acid is entirely opposed to the author's experience. He has repeated some of his experiments, which again prove that brucine only reacts with nitric acid, not with nitrous acid. If a reaction is obtained with a nitrite, this shows that the nitrous acid has been partly converted into nitric acid; a result that will always happen if the nitrous acid at the moment of its liberation does not come in contact with an excess of strong sulphuric acid so as to form the stable nitrosylsulphuric acid. If the directions given by the author and Lwoff (*Abstr.*, 1894, ii, 398) are carefully followed, nitrous acid cannot be mistaken for nitric acid.

I. DE K.

**Destruction of Organic Matter in the Analysis of Substances containing Phosphorus, Arsenic, and Metals.** By G. MEILLERE (*J. Pharm. Chim.*, 1902, [vi], 15, 97—99).—The destruction of the organic matter is effected by heating the substance with a small quantity of potassium sulphate and a mixture of 1 part of sulphuric acid and 4 parts of nitric acid by volume. The method is especially suitable for the estimation of phosphorus, lead, arsenic, mercury, copper, and zinc in the presence of organic matter. H. R. LE S.

**Detection of Phosphorus in Cases of Poisoning.** By P. E. ALESSANDRI (*L'Orosi*, 1901, 24, 397—407).—The best preliminary test for phosphorus in cases of suspected poisoning is that suggested by Bindz, consisting in dipping into the stomach contents, &c., a glass rod, which is then rubbed vigorously on a heated glass plate in a dark place; very minute quantities of phosphorus give a visible phosphorescence. A portion of the material may also be extracted with carbon disulphide, the solution being then evaporated and tested as follows: (1) By phosphorescence as above described. (2) By heating a small quantity of the residue dissolved in either carbon disulphide or alcohol and allowing the vapours evolved to impinge on slides moistened with (a) a nitric acid solution of molybdic acid, and (b) silver nitrate, the slides being afterwards examined under the microscope. (3) By microscopic examination of the residue from the carbon disulphide extract, in order to discover, if possible, small fragments of free phosphorus. (4) By inspection of the flame given by the alcoholic solution of the residue left from the carbon disulphide extract.

T. H. P.

**Detection and Approximate Estimation of Minute Quantities of Arsenic in Beer, Brewing Materials, Food-Stuffs, and Fuel.** By the Conjoint Committee of the Society of Chemical Industry and the Society of Public Analysts [OTTO HEHNER, ALFRED H. ALLEN, ALFRED C. CHAPMAN, CHARLES ESTCOURT, DAVID HOWARD, ARTHUR R.

LING, RUDOLPH MESSEL, and LEONARD T. THORNE] (*Analyst*, 1902, 27, 48—53).—*Procedure without destruction of organic matter*.—Beer is diluted with an equal volume of hydrochloric acid. Of malt, 50 grams are taken and extracted at 50° with a mixture of 50 c.c. of hydrochloric acid and 50 c.c. of water; 20 c.c. of the liquid then contain the arsenic from 10 grams of the sample. Of hops, 20 grams are digested with 100 c.c. of dilute hydrochloric acid (1:1), and 50 c.c. of the strained liquid are used for the test. Of brewing sugars, 10—20 grams are dissolved in water and 10 c.c. of hydrochloric acid added. If sulphites are present, these must be oxidised by bromine, the excess of which is then boiled off. *Destruction of organic matter. Acid method*.—Ten grams of the substance or the residue of 10—20 c.c. of beer are evaporated in a 3½ inch porcelain crucible with 10—15 c.c. of nitric acid on a sand-bath until no more brown fumes are evolved. Three c.c. of strong sulphuric acid are added and the heating continued until the mass begins to char, when another 5 c.c. of nitric acid are added. After completely expelling the acid, the crucible is half filled with water and a few c.c. of hydrochloric or dilute sulphuric acid and the charred mass is extracted for half-an-hour on the water-bath. The filtrate and hot washings are evaporated down to 30 c.c. and should be colourless. When testing hops, these should be gradually added to a mixture of 10 c.c. of nitric and 5 c.c. of sulphuric acid; when half the hops have been introduced, another 5 c.c. of nitric acid are added, when the whole is treated as before. *Basic method*.—Twenty c.c. of beer are evaporated with 1 gram of pure calcium or magnesium oxide; solid materials are mixed with half their weight of the same, and the mixture is incinerated. The ash is then dissolved in dilute acid and tested. The process is however, not recommended for hops. Of coal and other fuel, two portions of 1 gram each are taken, one being ignited without, and the other with, addition of 1 gram of either base. The difference in arsenic between the two determinations represents the volatile arsenic.

The final testing is effected in the Marsh apparatus, for the exact form of which the original article and illustration should be consulted. The arsenical mirrors are compared with those obtained by testing standard solutions containing 0.002, 0.004, 0.006, 0.008, and 0.01 mg. of arsenious acid per 2 c.c. Careful blank experiments should be made to make sure of the complete absence of arsenic in the reagents used.

L. DE K.

**Detection of Arsenic in Hydrochloric and Sulphuric Acids.**  
By E. SEYBEL and H. WIKANDER (*Chem. Zeit.*, 1902, 26, 50).—Five c.c. of hydrochloric acid or sulphuric acid (previously diluted to sp. gr. 1.45) are mixed with a few drops of a concentrated solution of potassium iodide. In the presence of arsenic in either state of oxidation, a yellow colour or turbidity due to arsenic triiodide is formed. If the sulphuric acid should contain lead, a precipitation of lead iodide may be prevented by adding some hydrochloric acid. Some impurities may be present which interfere with the reaction, for instance, free chlorine or ferric chloride in hydrochloric acid, or nitroso-compounds in sulphuric acid. The test will still show 1 part of arsenious acid in 100,000 parts of acid.

L. DE K.

**A Criticism of the Classical Method employed for the Separation of Traces of Arsenic and Antimony.** By LÉONCE BARTHE (*J. Pharm. Chim.*, 1902, [vi], 15, 104—109. Compare Abstr., 1901, ii, 690; this vol., ii, 52).—A critical review of the possible sources of error in the methods usually employed for the separation and estimation of traces of arsenic and antimony. H. R. LE S.

**Analysis of Commercial Copper and Mattes.** By P. TRUCHOT (*Ann. Chim. anal.*, 1902, 7, 58—61. Compare Abstr., 1901, ii, 197, and this vol., ii, 228).—*Estimation of selenium and tellurium.*—Keller's process (precipitation of selenium and tellurium by ammonia in the presence of ferric sulphate), as used in the smelting works in the western United States, is recommended. *Estimation of phosphorus.*—In Keller's process, this will remain in solution after the separation of tellurium, selenium, arsenic, &c., by hydrogen sulphide. After precipitating it by means of ferric chloride in the presence of calcium carbonate, it is finally separated by the molybdic acid process. *Estimation of sulphur.*—One gram of matte or about 5 grams of copper are treated by the method previously described (Abstr., 1900, ii, 309). *Estimation of gold and silver.*—Fifty to 100 grams of the sample of copper or matte are dissolved in 350—700 c.c. of nitric acid of sp. gr. 1.2, the insoluble matter is collected, ignited, and scorified with 5—6 grams of lead and some borax glass. The button of lead is finally cupelled in the ordinary way to obtain a button of gold. The acid filtrate containing the silver is mixed with 3 or 4 c.c. of sodium chloride solution, and the silver chloride so obtained is collected on a filter and incinerated with addition, if necessary, of some sodium hydrogen carbonate. The ash is then subjected to scorification with lead and subsequent cupellation. L. DE K.

**Analyses of Chromates and Manganates.** By W. HERZ (*Ber.*, 1902, 35, 949).—For the quantitative analyses of chromates and manganates, reduction by means of hydrazine sulphate instead of alcohol or hydrogen sulphide is recommended. R. H. P.

**"White Spirit."** By AMBROISE ANDOUARD and P. ANDOUARD (*J. Pharm. Chim.*, 1902, [vi], 15, 99—101).—Oil of turpentine is sometimes adulterated with an American petroleum known as white spirit. Such adulteration will be recognised by the fact that the oil of turpentine will have a blue fluorescence, a low rotatory power, and will not be completely volatile on exposure to air. H. R. LE S.

**Titration of Potassium Ferrocyanide with Potassium Permanganate.** By BRUNO GRÜTZNER (*Arch. Pharm.*, 1902, 240, 69—73).—When potassium permanganate is added to a dilute solution of potassium ferrocyanide, containing only a slight excess of sulphuric acid, in amount equal to about half that required for complete oxidation, a small quantity of a greyish powder is precipitated; this has the composition  $K_2MnFe(CN)_6$ .

If accurate results are to be obtained in titrating a ferrocyanide with permanganate, the concentration of the ferrocyanide in the

solution should be about 0.1 per cent., and plenty of sulphuric acid should be present. The permanganate solution should be standardised against pure potassium ferrocyanide, and in the actual estimation the same shade of colour should be taken to indicate the end-point as in the standardisation.

C. F. B.

**Estimation of Methoxyl Groups in Sulphur Compounds.** By FELIX KAUFLE (Monatsh., 1901, 22, 1105—1108).—This method is of use where the methoxyl group can be hydrolysed by potassium hydroxide, and may therefore be used to distinguish between methoxyl groups of esters and of ethers. The methoxy-compound is boiled with aqueous potassium hydroxide, and the alcohol vapour is carried by a current of air over ignited copper sulphate and absorbed in hydriodic acid kept cool by ice. The methyl iodide is afterwards distilled into silver nitrate solution. In this way, the formation of mercaptan in the hydriodic acid is avoided. Determinations with potassium methyl sulphate, dimethyl sulphate, methyl benzenesulphonate, and mono- and dimethyl sulphobenzoate gave good results.

G. Y.

**Mannitic Fermentation of Wine.** By PHILIP SCHIDROWITZ (*Analyst*, 1902, 27, 42—47).—A paper on the injurious effect of the mannitic fermentation of wines, and the means by which it can be avoided. The author estimates the mannitol by the process recommended by Gayon and Dubourg (*Ann. Inst. Pasteur*, 1901, 15, 527), as follows: 50 c.c. of the wine are evaporated on the water-bath to a syrup, with addition of 2—3 grams of sand, and then allowed to remain in a cool place for two or three days, when the mannitol will have crystallised. One hundred c.c. of 85 per cent. alcohol, saturated with mannitol at the temperature of the room, are added with constant stirring, and the whole is drained on a filter for two hours. The filter is then extracted in a Soxhlet apparatus for one hour with 100 c.c. of 85 per cent. alcohol,  $\frac{4}{5}$  of the alcohol is distilled off, the remainder decolorised with a little animal charcoal, filtered, and the residue washed twice with about 50 c.c. of hot 85 per cent. alcohol. The filtrate is evaporated to dryness at 60°, and the residual mannitol is weighed as such. If the wine contains much sugar, it is best to remove this by fermentation, before estimating the mannitol.

Mannitol may be tested for qualitatively by shaking the wine with yellow mercuric oxide, allowing a few c.c. of the filtrate to slowly evaporate, and examining the residue with the microscope. Characteristic fine, silky needles will then be observed.

L. DE K.

**Use of Acid Mercuric Nitrate in the Analysis of Sugar Solutions.** By GUSTAVE PATEIN and ÉMILE DUFAY (*J. Pharm. Chim.*, 1902, [vi], 15, 221—226).—The use of acid mercuric nitrate for decolorising sugar solutions has been objected to on the ground that the nitrate oxidises part of the sugar. It is now shown that if the author's method is followed in detail, the sugar present in the solution suffers no change whatever. A solution of mercuric nitrate, prepared by dissolving yellow mercuric oxide in the calculated quantity of

nitric acid, is mixed with the sugar solution to be decolorised, and a solution of sodium carbonate added until the liquid is no longer acid to litmus paper. The filtrate from this contains the whole of the sugar, together with a trace of mercuric nitrate, which must be removed by means of sodium hypophosphite if the sugar is estimated by means of Fehling's solution.

H. R. LE S.

**Drying of Carbohydrates and Estimation of their Water of Crystallisation.** By ERNST SCHULZE (*Chem. Zeit.*, 1902, 26, 7—8).—The carbohydrate is placed in a glass boat and introduced into a copper tube fixed into a copper trough containing brine or dilute glycerol, and heated at 100°, a current of dry hydrogen being transmitted for about an hour. In the case of raffinose, to prevent fusion, the temperature should at first not exceed 75°. Lactose does not part with all its water at 100°, although it may probably do so by protracted drying. The loss suffered by many carbohydrates, such as stachyose, at a more elevated temperature is not due to true water of crystallisation.

L. DE K.

**Estimation of Starch in Cereals.** By LÉON LINDET (*Ann. Chim. anal.*, 1902, 1, 41—43).—A modification of the author's process for the estimation of starch in cereals (*Abstr.*, 1897, ii, 525).

The ground cereal is treated as before with pepsin and hydrochloric acid, and the separated starch collected in a conical phial and washed by decantation. Instead of weighing the starch as such, it is now proposed to heat it with 100 c.c. of water, containing 0.25, 0.5, or 1 c.c. of sulphuric acid, for one hour at 110°; the acid is then neutralised with sodium hydroxide, and the liquid diluted to 250 c.c. The solution is titrated with Fehling's solution, which gives the amount of starch converted into dextrose; the solution is also examined in the polariscope, and after allowing for the rotatory power of the dextrose, the extra rotation is considered to be due to dextrin, which is then also expressed as starch.

L. DE K.

**Detection of Salicylic Acid in Foods.** By HENRI TAFFE (*Ann. Chim. anal.*, 1902, 7, 18—19).—The mixture of equal volumes of ether and light petroleum formerly proposed by the author is not sufficiently anhydrous and is therefore still capable of dissolving traces of tannins which interfere with the ferric chloride reaction.

It is now recommended to stir in, by means of a glass rod, an extra quantity of light petroleum before pouring off the ethereal layer. Any emulsion may be again treated with a fresh quantity of light petroleum.

L. DE K.

**Detection and Estimation of Methyl Anthranilate.** By ERNST ERDMANN (*Ber.*, 1902, 35, 24—27).—Methyl anthranilate readily yields a diazonium salt which combines with  $\beta$ -naphthol or  $\beta$ -naphtholdisulphonic acid R. The azo-colouring matter produced with  $\beta$ -naphthol is insoluble, and the reaction may be employed in the estimation of the ester in oil of jasmine or oil of neroli. The diazo-solution contained in a burette is run into an alkaline solution containing a known

weight of  $\beta$ -naphthol until a filtered sample neither reacts with the diazo-solution nor with an alkaline solution of the naphthol. Very small quantities of the ester may be thus estimated. The method is also available for mandarin oil, which contains methyl methylantranilate as well as the primary amino-ester; the extract is treated with excess of nitrous acid, the oily nitrosoamine of the secondary amino-ester is removed by means of ether, and the aqueous solution of the diazonium compound examined in the manner indicated.

G. T. M.

#### Detection of Drying Oils and Marine Animal Oils in Mixtures.

By GEORGES HALPHEN (*Ann. Chim. anal.*, 1902, 7, 5—8, 54—58).—The reagent used by the author consists of 5 volumes of glacial acetic acid, 1 vol. of nitrobenzene, and  $\frac{1}{2}$  vol. of bromine. One c.c. of the oil is mixed with 15 c.c. of the reagent, and both drying oils and fish oils give an insoluble bromine substitution product. This is collected on a filter, washed with ether, and then well pressed between "Papier Joseph." The dry mass is then heated to a temperature just below boiling with carbon tetrachloride (2.5 c.c. for each 0.1 gram). The precipitate derived from linseed oil dissolves completely, but on cooling it gradually deposits, forming an alumina-like, bulky, gelatinous substance. Fish oil yields an opalescent solution showing a white reflection on the sides of the tube; the opalescence increases on cooling, but only a trace of lustrous precipitate is formed. The same difference is observed by operating on the products obtained on repeated purification by alcohol.

Vegetable oils, such as linseed, hempseed, nut, and wood (? croton) oils, yield clear solutions, depositing on cooling a more or less abundant gelatinous precipitate; in the case of hempseed oil, this may take some hours and there is a danger of overlooking it. In the case of animal oils, such as seal, whale, cod-liver, shark-liver, and sperm oils, the solution of the bromine derivative in carbon tetrachloride is always opalescent, and yields but a trace of a crystalline precipitate.

*Improved Application of the Test.*—Twenty-eight c.c. of glacial acetic acid are mixed with 4 c.c. of nitrobenzene and 1 c.c. of bromine. 0.5 gram of the oil is mixed in a test-tube with 10 c.c. of the reagent, the tube is corked, gently shaken, and the effect observed.

1. Oils which do not give any precipitate sooner or later and remain clear even after an hour. *Vegetable oils*: olive oil, almond oil, castor oil, white earth-nut oil, cotton oil, and poppy oil; *Animal oils*: lard oil and neats-foot oil derived from oxen, sheep, and horses. 2. Oils which give no marked precipitate even after an hour, but give a slightly turbid solution. *Vegetable oil*: Joffa sesamé oil; *Animal oils*: some kinds of neats-foot oil derived from sheep and horses. 3. Oils which become turbid and gradually yield a precipitate, collecting more or less rapidly at the bottom of the tube. *Vegetable oils*: nut oil (precipitates after 5 or 10 minutes), hemp-seed oil, some kinds of linseed oil; *Animal oils*: Japanese fish oils, seal oil, shark oil, whale oil, and sperm oil. 4. Oil which causes a turbidity and separates on standing into two different liquid layers. Colza oil. The turbidity disappears at once on shaking with 10 c.c. of ether, but if the oil should contain 10

per cent. or more of drying oils, or fish oils an insoluble precipitate will be noticed.

Excepting colza oil, the oils may be divided into two classes; the first one containing the fish oils, and nearly the whole of the drying oils, and the other the non-drying oils and those from terrestrial animals. By the process described, mixtures containing 10 per cent., or even less, of the former may be easily recognised. To ascertain whether the precipitate is derived from a drying vegetable oil or a marine-animal oil, it is collected on a filter, washed with ether, pressed dry between "Papier Joseph," and then dissolved in boiling carbon tetrachloride, the filtrate being again boiled, and passed twice through the filter. The filtrate is evaporated to dryness in a tared dish. If the quantity should be rather small, it is dissolved in boiling carbon tetrachloride, and introduced into a previously graduated tube 15 cm. long and 4 mm. wide. The top part of the tube being heated, the liquid is boiled until for every 0.1 gram of precipitate 2.5 c.c. of solvent are left; the tube is then corked or sealed, and after three or four hours the contents are examined. If the brominated precipitate was due to a vegetable drying oil, the liquid will be either clear and thin with a gelatinous precipitate on the top, or this may occupy the whole of the volume. When due to the oil from marine animals, the liquid is white or yellowish and opalescent, with occasionally a trace of a brilliant lamellar precipitate. When due to neats-foot oil from terrestrial animals, the liquid is clear, non-opalescent, and free from gelatinous precipitate; occasionally, however, a slight turbidity is noticed.

Oils from marine animals are characterised by forming an immediate precipitate with the reagent; oils from terrestrial animals take a long time to deposit.

L. DE K.

**Estimation of the Iodine Number of Fats.** By C. A. JUNGCLAUSSEN (*Chem. Centr.*, 1901, ii, 1324; from *Apoth. Zeit.*, 16, 798).—Hanuš's method (this vol., ii, 112) is strongly recommended. When operating on about 0.13 gram of cod liver oil the iodine number was 141.5 after a quarter of an hour; 146.2 after half-an-hour; 151.6 after an hour; 152.14 after 2 hours, and 153.74 after 10 hours. The author thinks that the action is complete after 4 hours.

L. DE K.

**Japan-Tallow.** By OSCAR BERNHEIMER and F. SCHIFF (*Chem. Zeit.*, 1901, 25, 1008).—A specimen of unadulterated Japan-tallow, having the usual melting point (52.6—53.4°) and saponification number (220—222), may yet have an iodine number (10.5—11.3) higher than the normal value (4.2), and an acid number (11.4—14) lower than the normal value (20).

K. J. P. O.

**Method for the Separation of Organic Bases from their Phosphotungstic Acid Precipitates and the Behaviour of Cystine to Phosphotungstic Acid.** By ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1901, 34, 153—156).—Instead of decomposing the phosphotungstate precipitate with barium hydroxide, the author recommends shaking it with ether and hydrochloric acid. Three layers are thus obtained, at the top aqueous ether, at the bottom a



syrupy ethereal solution of phosphotungstic acid, and between them an aqueous solution of the hydrochlorides of the bases. The operation is repeated and the combined aqueous solutions evaporated. Good results can be obtained. According to the author, cystine is slowly precipitated by phosphotungstic acid, as is also cysteine, the latter, however, probably as cystine (compare Mörner, *Abstr.*, 1900, i, 128).  
J. J. S.

**Detection of Cocaine.** By HANS PROELSS (*Chem. Centr.*, 1901, ii, 1321; from *Apoth.-Zeit.*, 16, 779—781, 788—789. Compare *Abstr.*, 1901, ii, 706).—Cocaine cannot be detected in organs after about 14 days, as it is converted into ecgonine, which cannot be extracted by means of an immiscible solvent either from an acid or alkaline solution, and is not precipitated by the ordinary alkaloidal reagents; moreover, there is no characteristic test for ecgonine. A really trustworthy test for cocaine itself is still a *desideratum*; the best test as yet proposed is based on the reduction of mercurous chloride.  
L. DE K.

**Resistance of Morphine to Putrefaction.** By THEODOR PANZER (*Zeit. Nahr. Genussm.*, 1902, 5, 8—10).—The author succeeded in proving the presence of morphine in organs (part of large and small intestine, stomach and contents, liver, kidney) after these had been drenched with water and kept for 6 months in a loosely covered beaker.

The amyl alcohol extract obtained in due course was, as might have been expected, very much contaminated with objectionable matter. To purify the mass, it was treated with dilute hydrochloric acid and the extract shaken with amyl alcohol, which removed nearly all the colouring matter. The acid solution was now rendered alkaline with ammonia and shaken with pure ethyl acetate; this, on spontaneous evaporation, yielded an amorphous mass which completely dissolved in dilute hydrochloric acid. This solution soon deposited colourless needles which gave all the reactions for morphine; in another experiment, however, it was found necessary to decolorise the solution with animal charcoal.  
L. DE K.

**The Proteids of Urine.** By A. HERLANT (*Chem. Centr.*, 1902, i, 141—142; from *Bull. assoc. belge Chimistes*, 15, 311—313).—Mucin may be precipitated by adding to the urine 1/20 part of acetic acid and heating for an hour at 30—40°. The only safe test for albumin is the boiling test; when the sp. gr. of the sample falls below 1.015, 2—3 per cent. of sodium chloride or sulphate should be added. Trichloroacetic acid is preferable to ordinary acetic acid. Serum-albumin and globulin are precipitated as usual with magnesium sulphate.

The biuret reaction is obtained with albumin as well as with albumoses and peptones. The author first precipitates the albumin, heats the filtrate with zinc sulphate at 30—40°, and estimates the nitrogen in the zinc precipitate by Kjeldahl's process; multiplied by 6.25, this represents albumoses. If the filtrate should again give the biuret reaction, peptones are present, the exact estimation of which is very difficult.

Organised sediments may be freed from adhering urate deposits by adding to the sample 1/20 of its volume of formaldehyde.

L. DE K.

**Detection of the Colouring Matters of the Blood in Urine.** By OTTO ROSSEL (*Chem. Centr.*, 1902, i, 142; from *Schweiz. Wochschr. Pharm.*, 39, 557—558).—The sample is strongly acidified with acetic acid, agitated with an equal volume of ether, and any emulsion removed by adding a drop of alcohol. The ethereal layer is then transferred to another test glass containing a few drops of water. Fifteen to twenty drops of old oil of turpentine and five to ten drops of fresh hydrogen peroxide are added, and after gently shaking, ten to twenty drops of a freshly prepared 2 per cent. alcoholic solution of Barbadoes aloes are also added, and the whole vigorously shaken. In the presence of a trace of blood so small that it cannot be proved spectroscopically, the aqueous layer assumes, after 1—3 minutes, a reddish colour, which after 10 minutes turns to a beautiful cherry-red.

L. DE K.

**Forensic Detection of Blood by means of Alkaline Hæmatoporphyrin.** By ERNST ZIEMKE (*Chem. Centr.*, 1901, ii, 1322; from *Vierteljahrschr. ges. Med. u. öffentl. Sanitätswesen*, 22, 231—234).—The material suspected to contain blood stains is finely divided, put into a beaker, and covered with sulphuric acid. After 24 hours, the acid is filtered through glass-wool, diluted with four times its bulk of water, and neutralised with ammonia. The precipitate is washed several times by decantation, collected on a filter, air-dried, rubbed with a mixture of equal parts of alcohol and ammonia, and filtered. The filtrate forms a more or less dark red liquid, which shows the characteristic four-banded spectrum of alkaline hæmatoporphyrin; if the liquid is too concentrated, the bands in the violet are lost in the general absorption which takes place. If the liquid is too dilute, it must be concentrated, or thicker layers employed. When the filtrate is poured drop by drop into strong sulphuric acid, the resulting solution also shows the spectrum, but not so plainly as in alkaline solution.

L. DE K.

**Ehrlich's *p*-Dimethylaminobenzaldehyde Reaction.** By CLEMENS (*Chem. Centr.*, 1901, ii, 1320; *Deutsch. Arch. Klin. Med.*, 71, 168—174).—*p*-Dimethylaminobenzaldehyde gives a cherry-red coloration of varying intensity, even with previously boiled normal urine, the colouring matter is partly soluble in chloroform and completely in epichlorohydrin and dichlorohydrin. The author has tried the action of the reagent on a number of pathological urines and comes to the conclusion that the reaction is not caused by any components of either normal or pathological urine already known. The fact that urines which give the reaction do not show an increased reducing power does not tally with Pröscher's theory that the colouring matter may be a formyl-glucosamine or an acetyl derivative of an unknown pentosamine; moreover, the test is not given by glucosamine, lævulosamine, or lactosamine.

L. DE K.

## General and Physical Chemistry.

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**Decomposition of Hydrogen Peroxide by Light, and the Electrical Discharging Action of this Decomposition.** By R. F. D'ARCY (*Phil. Mag.*, 1902, [vi], 3, 42—52).—A solution of hydrogen peroxide is decomposed much more rapidly when exposed to the sun than when kept in diffuse light. Under the influence of sunlight, a surface of hydrogen peroxide loses a negative charge of electricity more rapidly than a similar water surface. This action of light on hydrogen peroxide is regarded as a possible origin of the electrically charged particles present in the air. J. C. P.

**Radioactive Substances.** By F. HENNING (*Ann. Phys.*, 1902, [iv], 7, 562—575).—The first part of the paper is a study of the radioactivity induced in metal wires by thorium oxide (see Rutherford, Abstr., 1900, ii, 352) in its dependence on the surface area of the wires, the volume of the containing tube, the fall of potential, and the thickness of the inducing layer of thorium oxide.

An attempt was also made to distinguish the conductivities of radioactive and ordinary barium chlorides, but with no very definite result. J. C. P.

**Absorption of Röntgen Rays by Aqueous Solutions.** By R. K. McCLUNG and DOUGLAS McINTOSH (*Phil. Mag.*, 1902, [vi], 3, 68—79).—By an electrical method, more accurate probably than the photographic method used by other investigators, the authors have shown that (1) the absorption of Röntgen rays by water is independent of the temperature; (2) the absorption by a salt solution increases with the concentration, the connection between the two being of a logarithmic character; (3) the absorption by anions and cations increases generally with the atomic weight (compare Blythwood and Marchant, Abstr., 1900, ii, 182). It has further been found that the absorption in colloidal solutions of lead, mercury, and silver (see Bredig, Abstr., 1900, ii, 213), differs very slightly, except possibly in the case of mercury, from that in pure water. J. C. P.

**A Kind of Radioactivity imparted to certain Salts by Cathode Rays.** By J. C. McLENNAN (*Phil. Mag.*, 1902, [vi], 3, 195—203).—A number of salts, namely, the sulphates and sulphides of barium, strontium, and calcium, and potassium sulphate, exhibit marked radioactivity after being exposed to the action of cathode rays; to produce the effect, the salts must be heated to at least 100°, but the radioactivity is more marked at still higher temperatures. It is shown that this radioactivity is not due to the action of ultra-violet light, and has apparently no connection with the phenomenon of thermoluminescence. The heating of the excited salts may be regarded as producing ultra-violet light or as leading to the emission of a stream of negatively charged particles. J. C. P.

**Conductivity of Liquid Dielectrics under the Influence of Radium or Röntgen Radiations.** By P. CURIE (*Compt. rend.*, 1902, 134, 420—423).—It is shown that liquid dielectrics, like gases, acquire conductivity under the influence of radium or Röntgen radiations, results of the same order of magnitude being obtained in the two cases. In the case of gases, the intensity of the current increases proportionally to the difference of potential between the electrodes when this difference is slight, but becomes almost constant when the difference is increased sufficiently. In the case of the liquids, however, the proportionality exists up to a potential difference of 450 volts. Of the liquids examined, carbon disulphide gave the greatest conductivity, which reaches  $20 \times 10^{-14}$  mhos per 1 c.c. Liquids which are ordinarily almost perfect non-conductors exhibit this effect, as, for example, liquid air, light petroleum, &c. The effect was exactly the same whether the radium was kept at the ordinary temperature or at the temperature of the liquid, from which it follows that the radiation from the radium does not vary with temperature between the limits of the ordinary temperature and that of liquid air.

L. M. J.

**Some Measurements with Gas Elements.** By VINCENT CZEPINSKI (*Zeit. anorg. Chem.*, 1902, 30, 1—17).—The high *E.M.F.* observed by Bose (Abstr., 1900, ii, 704) with the hydrogen | oxygen element has been confirmed, but the author does not agree with Bose and Wilsmore (Abstr., 1901, ii, 2) as to this being due to the formation of hydrogen peroxide or persulphuric acid; it is rather to be attributed to the depolarising action of the oxygen dissolved in the electrolyte and to diffusion of the gas.

It has been found that methane is totally indifferent in an electromotive respect when opposed to a hydrogen electrode, and measurements have been made with the element  $\text{Pt} | \text{H}_2 + \text{CH}_4 | \text{H}_2\text{SO}_4, \text{aq} | \text{H}_2 | \text{Pt}$ . The pressure of the hydrogen in the methane and hydrogen mixture varied from 0.004 to 0.11 atmosphere, and the arrangement is a true gas concentration element. The *E.M.F.* should be  $E = (0.000198T)/2 \cdot \log(P/p)$ , where  $P$  is the pressure of the pure hydrogen (1 atmo.) and  $p$  the partial pressure in the mixture. With the most dilute mixtures, the *E.M.F.* has too high a value at first, but this rapidly falls and an equilibrium is reached, although the observed *E.M.F.* does not agree well with that calculated. At the higher concentrations (4 and 11 per cent. of hydrogen in the mixture), the *E.M.F.* is at first too low, but it slowly rises and becomes constant at a value which is in very close agreement with that calculated.

The irregularities noticed with the mixtures of low hydrogen concentration are attributed to the depolarising influences of traces of oxygen dissolved in the electrolyte.

J. McC.

**Electromotive Force of the Hydrogen Chlorine Element.** By ERICH MÜLLER (*Zeit. physikal. Chem.*, 1902, 40, 158—168. Compare Abstr., 1901, ii, 537).—The *E.M.F.* of the element was determined in an apparatus similar to that used by Wilsmore (Abstr., 1901, ii, 2); the electrolyte was hydrochloric acid solution and the gases were con-

tinuously passed over the electrodes. The following values were obtained for the *E.M.F.* with the various concentrations of acid :

Normality of acid .. .. .	1	1/10	1/100	1/1000
<i>E.M.F.</i> .. .. .	1.3660	1.4849	1.5460	1.5868 volts.

Assuming that *N*-hydrochloric acid is dissociated to the extent of 78 per cent., it is calculated that the electrolytic potential is 1.3532 volts.

The observed values of the *E.M.F.* are not in agreement with those calculated, and it is shown that this is partly due to the hydrolysis of the chlorine which takes place, and this increases the concentration of the  $H^+$  and  $Cl^-$ . In *N*/10 solution of hydrochloric acid, the  $H^+$  or  $Cl^-$  concentration rises from 91 to 94.03 millimols. per litre by this hydrolysis, in *N*/100 solution from 9.6 to 33.48, and in *N*/1000 solution from 0.98 to 30.48. With the aid of these concentration differences, the calculated values of the *E.M.F.* agree better with the observed values, but the deviations remain greater than the experimental error.

The origin of the chlorine (hydrochloric acid and dichromate, hydrochloric acid and pyrolusite, or electrolytic) has no influence on the *E.M.F.*, and heating the gas in order to decompose chlorine peroxide is also without influence.

J. McC.

**Conductivity of Solutions of Mixed Electrolytes.** By HANS WOLF (*Zeit. Elektrochem.*, 1902, 8, 117—119).—The conductivity of a mixture of two electrolytes differs from the sum of the conductivities of the electrolytes singly on account of (1) the change of viscosity of the solution ; (2) decreased dissociation, due to replacement of water by the other electrolyte ; (3) chemical reaction between the electrolytes. For solutions containing a small quantity of potassium chloride or sodium bromide and variable quantities of acetic acid or alcohol, the first action is alone of importance ; with stronger solutions (0.5 normal), the second comes into play.

When chloroacetic acid is used in place of acetic acid, the matter is further complicated by the occurrence of the chemical reaction to an appreciable extent. The conductivity of zinc sulphate is diminished to a greater extent by acetic acid or alcohol than is that of potassium chloride. Tartaric acid has an effect similar to that of acetic acid, except in the case of zinc sulphate, the conductivity of which is but little affected. This is doubtless due to the formation of hydrogen ions in place of zinc ions, which increase the conductivity almost as much as it is diminished by the increased viscosity. Mixtures of the salts of fatty acids with fatty acids were also examined ; in these cases, the chemical change can be calculated and allowed for ; the remaining change of conductivity is found to be very similar to that observed in the case of sodium bromide and acetic acid.

T. E.

**Faraday's Law and its Range of Validity.** By EMIL BOSE (*Chem. Zeit.*, 1902, 26, 47—48, 66—68).—From a consideration of the accurate measurements which have been made with the copper and with the silver voltameter, the author concludes that the slight deviations from Faraday's law are only apparent. To test the accuracy of the law, a salt may not be used the cation of which is

capable of existing in two forms, for then there enters a possible disturbing factor due to the reaction  $M^{\cdot\cdot} + M = 2M^{\cdot}$ . The deviations found in the electrolysis of silver salts (1/10000 of the total weight of silver) are due to secondary reactions, an important one of which is attributed to oxygen occluded by the platinum electrode. Faraday's law, so far as the weight of substance deposited by a given amount of electricity is concerned, may be regarded as an absolutely exact law of nature.

From the work of Ostwald and Nernst, it is shown that we may rightly conclude that the current which passes through an electrolyte is entirely conducted by transport of material, and there is no evidence of "metallic conduction."

The author regards Faraday's law as comparable with Dalton's law of multiple proportions so far as exactitude is concerned, and views it as an extension of Dalton's atomic laws. J. McC.

**Ionisation, Ionic Velocities, and Atomic Sizes.** By WILLIAM SUTHERLAND (*Phil. Mag.*, 1902, [vi], 3, 161—177).—This theoretical paper, which is a contribution to the solution of the difficulties of the ionic theory, deals with the following points: (1) the cause of ionisation; (2) the laws of ionisation in binary electrolytes; (3) the connection between the ionic velocities and other physical properties of the atoms. It is shown that high dielectric capacity, molecular association, and ionisation in water may all be deduced from the latent or potential valency of oxygen. According to the author, a molecule of water (represented as  $\#O\frac{1}{2}(\#H)_2$ , where  $\#$  is a positive,  $\frac{1}{2}$  a negative, electron) is a radicle with electric charges, yet not an ion, because the charges are equal and opposite. Such a radicle is called a stion, and the fact that certain substances do not conform to the law  $K=n^2$  is due to their containing stions, which are doublets of very large electric moment. In dealing with the laws of ionisation, the author lays stress on the part played by the viscosity of solutions. Further, the electron of the ion must be regarded as embedded in the ion, which will have a dielectric capacity different from that of the solvent; before ionisation can be satisfactorily determined, it will be necessary to have a thorough experimental investigation of the dielectric capacity of solutions. Ostwald's dilution law for acetic acid, it is suggested, may be merely the expression of equilibrium between the molecules  $(CH_3 \cdot CO_2H)_2$  and  $CH_3 \cdot CO_2H$ . Acetic acid probably exists in water in the form of double molecules; these are partly dissociated into  $CH_3 \cdot CO_2H$  molecules, and the latter are practically all ionised at the dilutions of Ostwald's experiments. J. C. P.

**New Apparatus for Determining the Relative Velocities of Ions; with some Results for Silver Ions.** By WILLIAM T. MATHER (*Amer. Chem. J.*, 1901, 26, 473—491).—The apparatus consists of two upright tubes about 18 cm. long and 2 cm. in diameter, on the upper ends of which are sealed tubes 6 cm. long and 0.5 cm. in diameter, these narrow portions being graduated in millimetres. Near the upper ends, the wide tubes are connected by a U tube, 0.5 cm. in diameter, provided at the middle with a stop-cock, and reaching to about 2 cm. above the lower ends of the wide tubes. The

electrodes, discs of silver, are introduced into the lower ends of the wide tubes. The advantages of the apparatus are that being symmetrical the current can be passed in either direction, that as it contains a large quantity of liquid a considerable change of concentration can be obtained, that the solution can be completely separated at the close of the electrolysis into two portions of accurately determined amount, and that the possibility of diffusion is small. The apparatus must be properly levelled.

The concentration change on electrolysis of aqueous and alcoholic solutions of silver nitrate and aqueous silver acetate has been determined at various temperatures and the following results obtained for the velocity ( $a$ ) of the anion: 0.1*N* silver nitrate in water at 0°,  $a=0.5411$ ; at 47.4°,  $a=0.5286$ ; and at 29.1°,  $a=0.5317$ . 0.025*N* silver nitrate in water at 0°,  $a=0.5377$  and at 45°,  $a=0.5246$ . 0.025*N* silver acetate in water at 0°,  $a=0.3734$ ; at 28.3°,  $a=0.3818$ ; at 44.7°,  $a=0.3896$ ; and at 49.4°,  $a=0.3873$ . 0.10805*N* silver acetate in alcohol (absolute) at 20°,  $a=0.594$ . 0.1*N* silver nitrate in 49.7 per cent. alcohol at 23.7°,  $a=0.5323$ . The author also calculates the absolute velocities of the silver and nitrate ions in water at different concentrations and at various temperatures. The differences between the velocities at 0° become less as the temperature rises. The effect of decrease of concentration is the same as that of increase of temperature. The results also show that the relative velocities are largely dependent on the nature of the solvent.

J. McC.

**Researches on Ionised Gases.** By P. LANGEVIN (*Compt. rend.*, 1902, 134, 414—417).—Experiments have been made the results of which are in complete accord with J. J. Thomson's views regarding the cause of the conductivity of gases under the influence of cathodic, &c., radiations. The experiments are not described, and the results only briefly indicated; the most important of these appear to be a proof of the recombination of the charged ions and a measurement of the ratio of the number of recombinations to the number of collisions between ions of opposite signs. This ratio, in accord with theory, is always less than unity, to which it approaches the more nearly when the mobility of the ions is small. The author states that he has obtained a method for the determination of the mobilities of the ions for different gases, and the absolute value of the recombination coefficient  $a$ , in the expression  $dp/dt = dn/dt = -apn$ , where  $p$  and  $n$  are the concentration of positive and negative ions.

L. M. J.

**Instantaneous Chemical Reactions and the Theory of Electrolytic Dissociation.** By LOUIS KAHLENBERG (*J. Physical Chem.*, 1902, 6, 1—14).—It has generally been supposed that instantaneous chemical reactions are dependent on the presence of ions, but the author has found cases of double decomposition accompanied by immediate precipitation in solutions which are excellent insulators. Copper, nickel, and cobalt oleates are easily soluble in benzene, giving solutions that are greenish-blue, green, and dark red respectively; these solutions conduct an electric current no better than pure benzene. Sodium, magnesium, aluminium, and zinc may be kept for weeks in

the copper oleate solution without any change taking place. Cryoscopic and ebullioscopic determinations give values for the molecular weight of copper oleate varying from 2342 to 2750, so that the salt must be polymerised. A solution of dry hydrogen chloride in benzene conducts no better than pure benzene, does not dissolve dry sodium, calcium, or barium carbonate, and does not attack iron or magnesium (zinc, however, is attacked). When such a solution is added to the oleate solutions referred to above, the metals are instantly and quantitatively precipitated as chlorides; the same result is attained if a current of dry hydrogen chloride is passed into the oleate solutions. Further, it is shown that stannic chloride, phosphorus and arsenic trichlorides, and silicon tetrachloride, which are all soluble in benzene to non-conducting solutions, precipitate cupric chloride from benzene solutions of copper oleate, the greatest care being taken, in this as in all cases, to exclude moisture. The oleates of copper, nickel, and cobalt are decomposed by hydrogen sulphide in benzene solution; stannic chloride and arsenic trichloride, treated with hydrogen sulphide in benzene solution, form sulphides only slowly. A solution of hydrogen chloride in benzene, and a solution of ammonia in benzene, both insulating as well as pure benzene, give instantly, when mixed, a white, bulky precipitate of ammonium chloride. The hydrochloride of pyridine may be precipitated in a similar manner. J. C. P.

**Condensation of the Vapours of Organic Liquids in Presence of Dust-free Air.** By FREDERICK G. DONNAN (*Phil. Mag.*, 1902, [vi], 3, 305—310).—Wilson has shown (*Abstr.*, 1898, ii, 372) that the condensation of water vapour in dust-free air is intimately connected with the presence of electrical nuclei. If now a solvent possesses ionising power because its molecules have an affinity for electrons, it is to be expected that the vapour of an ionising solvent will condense in dust-free air more readily than the vapour of a non-ionising solvent. This conclusion has been tested by Wilson's method, but the results are not very decisive. In several cases, condensation took place less readily with non-ionising solvents; on the other hand, carbon disulphide was very easily condensed, whilst acetone, a solvent of moderate ionising power, condensed only with difficulty. J. C. P.

**Apparatus for Heating by Electricity.** By ANTOINE GUNTZ (*Bull. Soc. Chim.*, 1902, [iii], 27, 153—158).—The author describes a method of fitting up apparatus for heating tubes, crucibles, &c., by means of electricity, the heat being obtained, as in other cases, by passing a current through a thin platinum wire. The improvement, however, is introduced of employing a mixture of magnesia and alumina for embedding the platinum wire in place of asbestos or fusible enamel, which possess the drawback that they alter the platinum wire when the temperature is raised to 1200—1300°. Particulars are given as to the management of such a heating arrangement and of the current which may be used with it, and the author states that he finds this apparatus more economical than gas. A. F.

**Measurement of Critical Constants.** By PHILIPPE A. GUYE and ED. MALLET (*Arch. Sci. phys. nat.*, 1902, [iv], 13, 274—296).—A



continuation of previous papers (this vol., ii, 242). The experimental results are now given, and are contained in the accompanying table, where  $T_c$  is the critical temperature,  $P_c$  the critical pressure,  $\mu$  the index of refraction for the  $D$  line at the temperature indicated, and  $D$  the sp. gr. at the temperature indicated, and  $\eta$  the coefficient of viscosity :

	$T_c$ .	$P_c$ .	$\mu$ .	$D$ .	$\eta$ .
Durene .....	402.5°	28.6			
Hexamethylbenzene..	> 478	—			
Diphenylmethane ...	497	28.2			
Diphenyl .....	495.6	31.8			
Naphthalene .....	468.2	39.25			
Anisole .....	368.5	41.2	1.5173 (20.6°)	0.9918 (20.6°)	0.01039 (22.3°)
Phenetole .....	374	33.8	1.5076 (21°)	0.9657 (21°)	0.01172 (23.4°)
<i>m</i> -Cresol .....	432	45	1.5418 (13.6°)	1.0384 (14.3°)	0.16767 (21.1°)
Aniline .....	425.6	52.3	1.5848 (22°)	1.0184 (22°)	0.0405 (22°)
Dimethylaniline .....	414.7	35.5	1.5565 (23°)	0.9537 (23°)	0.0137 (21.6°)
Dimethyl- <i>o</i> -toluidine	394.8	30.8	1.5248 (23°)	0.9255 (23°)	0.01489 (22.6°)
Piperidine .....	—	45.9	1.4530 (20.7°)	0.8602 (20.7°)	0.01554 (19.6°)
Acetonitrile .....	270.1	47.7	1.3417 (23.6°)	0.7785 (23.6°)	0.003466 (23.1°)
Propionitrile .....	285.7	41.3	1.3640 (24.6°)	0.7765 (24.6°)	0.004267 (21°)
Butyronitrile .....	309.1	37.4	1.3816 (24°)	0.7872 (24°)	0.005717 (22.3°)
Capronitrile .....	348.8	32.1	1.4048 (22.2°)	0.7990 (22.2°)	0.00942 (22°)
Benzonitrile .....	426.2	41.6	1.5272 (23°)	1.0016 (23°)	0.01316 (20.9°)
Propionic acid .....	326.8	—	1.3865 (21.4°)	0.9926 (21.4°)	0.01081 (23.2°)
Ethylchloroformate...	< 235	—	1.3949 (21.2°)	1.1334 (21.2°)	0.00545 (21.1°)

An attempt was made to determine the critical temperature of water, but at 345° the tube burst, and the fragments showed that, although the experiment had lasted but a short time, the water had attacked the glass very considerably. In a number of cases, the values given for the sp. gr., refraction, and viscosity have been taken from the results of other observers ; they are, however, added for completeness, and were in many cases obtained with the specimens employed by the authors.

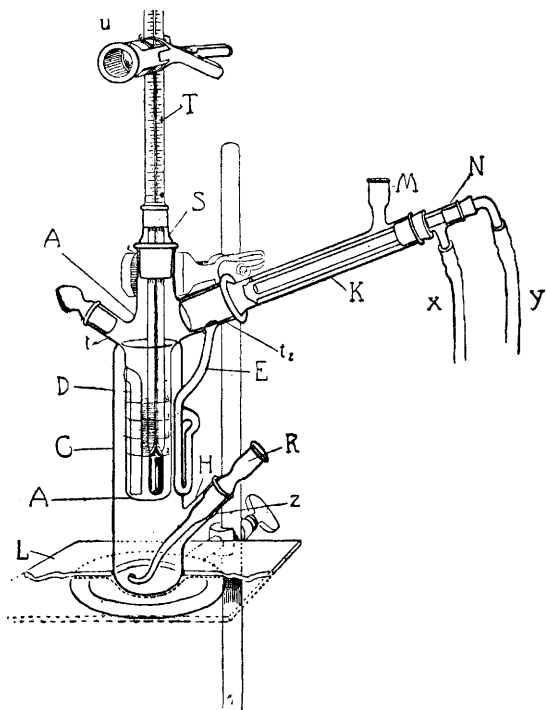
L. M. J.

**Determination of Molecular Weights. V. Further Development of the Boiling Point Method.** By ERNST BECKMANN (*Zeit. physikal. Chem.*, 1902, 40, 129—157. Compare Abstr., 1890, 323 ; 1891, 389, 1317 ; 1895, ii, 154 ; and 1897, ii, 88).—Details are given of the precautions which must be taken in using the author's boiling point apparatus in order to avoid errors on account of superheating. The amount of platinum or silver tetrahedra to be introduced in order to ensure even boiling is about 10 to 15 grams ; in place of this, 1 to 2 grams of metal and 10 to 15 of garnet crystals (such as are used for taring purposes) may be employed.

The Landsberger method is compared with the author's, and it is pointed out that the advantages lie on the side of the latter in so far as time of observation is concerned. In Landsberger's method, too, a great deal more solvent is required.

A modified form of apparatus is described where the solution is

heated by a current of vapour of the solvent. The ordinary Beckmann boiling tube, *A*, is provided with an internal tube, *D* (7 mm. diameter), fused into the side and passing to the bottom. The boiling tube is sealed into the wider vessel, *C*, at a point above the opening of the inner tube.



The outer vessel is provided with a tubulus, *R*, for supplying it with solvent, and through the tubulus a safety tube is inserted. Vapour evolved from the solvent in the outer vessel passes through the narrow tube into the boiling tube containing the thermometer, *T*. The condensed vapour may be allowed to flow back either to the boiling tube or, through a tube, *E*, which is sealed on, to the outer vessel. No solid material need be added to produce even ebullition.

The volume of the solution can be ascertained in the same way as has been described by Walker and Lumsden (*Trans.*, 1898, 502). Results are given to prove the efficiency of the apparatus.

J. MCC.

**Specific Volumes of Oxygen and Nitrogen Vapour at the Boiling Point of Oxygen.** By JAMES DEWAR (*Proc. Roy. Soc.*, 1902, 69, 360—366).—By determining the vapour densities of oxygen and nitrogen at the boiling point of the former, the author has further tested the validity of the method previously employed in finding the boiling point of hydrogen and oxygen (*Abstr.*, 1901, ii, 308). The specific volume of oxygen at 90.5° absolute and 760 mm. pressure is found to be 226 c.c.; from Regnault's density of oxygen at 0° and 760 mm. pressure, the value calculated according to the gaseous laws would be 231.8 c.c.; it thus appears that the product  $pv$  is diminished at the boiling point of oxygen by 2.46 per cent. It is noted that the value thus directly found for the specific volume of oxygen is quite different from the value 358 arrived at indirectly by Behn (*Abstr.*,

1900, ii, 260). The weight of a litre of oxygen at  $90.5^{\circ}$  absolute and 282.5 mm. pressure is 1.5982 grams, a smaller value than that calculated from the change of pressure. Nitrogen at its boiling point ( $78^{\circ}$  absolute) appears to deviate from the gaseous laws about as much as oxygen; from measurements of its vapour density at the boiling points of oxygen and air, the specific volume of nitrogen at  $78^{\circ}$  is calculated to be 221.3 c.c. J. C. P.

**Possible Significance of Changing Atomic Volume.** By THEODORE W. RICHARDS (*Zeit. physikal. Chem.*, 1902, 40, 169—184. *Proc. Amer. Acad.*, 1901, 37, 3—17).—Great compression of a substance may be due to two causes, one applied from outside, the other due to mutual internal attraction or affinity of the smallest particles for each other. The small compressibility of liquids and solids may be taken as evidence of a great compression of this second kind, and a study of the volume-changes in these cases might lead to some knowledge of the affinities at work. From the change of volume on mixing liquids, it may be gathered that similar liquids exhibit less change than dissimilar ones do; when the affinity of a substance for itself is not unlike that of the substance for another, no great change of volume occurs on mixing.

From the molecular volumes of several oxides, it is shown that the atomic volume of oxygen is not constant but is dependent on its environment; it is a function of the temperature and pressure and probably also of the electric stress. The stress under which a single substance rests may be measured by the work which heat is able to do on it, and this stress is given by  $P = Cdt/dv$ , where  $C$  is the molecular heat capacity,  $v$  is the volume, and  $t$  the temperature. The value of this stress is calculated for a number of metals, and it is concluded that there is a connection between the compression of substances and their tendency to combine with one another. From the tables of molecular volumes of chlorides and hydroxides, it is seen that when substances are arranged in the order of the contraction which ensues when hydroxyl combines with the metal, the same series is obtained as in the electrochemical order. This leads to the conclusion that the solution tension of a metal is associated with the excess of affinity of the metal for hydroxyl over its affinity for itself. This point is discussed in connection with formation of ions in aqueous solution. In aqueous solution, it is highly probable that the water as well as the salt must contract.

Chemical affinity is possibly a reciprocal function of mass, and in order to agree with the author's views, the atomic hypothesis must be modified so that the compressible environments ("atomic shell") around the centres of gravity and affinity are not so entirely disregarded as usual. J. McC.

**Dissociation of the Hydrate and Alcoholate of Chloral in Solution.** By LUDWIK BRUNER (*Bull. Acad. Sci. Cracow*, 1901, 464—473).—In order to determine whether dissociation occurs during the dissolution of chloral hydrate and alcoholate in various solvents, the molecular increase of the boiling point was determined in solutions

in ethyl ether, acetone, methyl iodide, ethyl bromide, and carbon disulphide. A normal rise of boiling point was in all cases obtained, but with the last three solvents anomalous results were obtained; with chloral hydrate, the boiling point at first falling and afterwards slowly rising to a final value. This the author explains by the assumption of a partial dissociation, when, owing to the very slight solubility of the water produced, a two phase system results (although not apparent owing to the small quantity of water); this causes a lowering of the boiling point. The aqueous phase, however, soon distils off and the final higher value results. Cryoscopic experiments in nitrobenzene and in *p*-toluidine also lead to normal molecular weights, these solvents never differing from acetic acid in this respect (Beckmann, Abstr. 1891, 389). As chloral hydrate is partially dissociated when vaporised, the author calculated the latent heat of vaporisation from the molecular depression in chloral hydrate solutions and obtained the value 128·8 cal., which agrees well with the direct determination 132·4 cal., so that the van't Hoff expression  $\text{Mol. } D. > 0\cdot02 \text{ } T/L$  appears to hold even for compounds which partially dissociate when vaporised.

L. M. J.

**Solubility and Dissociation of Double Salts in Water.** By EBERHARD RIMBACH (*Ber.*, 1902, 35, 1298—1309. Compare Abstr. 1898, ii, 158).—The transformation point of a double salt has already been shown to be the temperature at which the two solutions saturated respectively with the double salt and one of its components become identical.

The double salt,  $4\text{NH}_4\text{Cl}, \text{CdCl}_2$ , decomposes into  $\text{NH}_4\text{Cl}, \text{CdCl}_2$  and  $\text{NH}_4\text{Cl}$ , and an examination of the solubility curves of the systems, double salt +  $\text{NH}_4\text{Cl}, \text{CdCl}_2$ , and double salt + ammonium chloride showed that these curves converge at a temperature approximately equal to  $-20^\circ$ ; this result is obtained, however, only by extrapolation.

Rubidium chloride combines with cadmium chloride to yield the double salt  $\text{RbCl}, \text{CdCl}_2$ , which separates in anhydrous, rhombic crystals. In this respect, rubidium and ammonium are analogous and they both differ from potassium, which gives rise to the salt  $\text{KCl}, \text{CdCl}_2, \text{H}_2\text{O}$ . The solubilities of the double rubidium salt are tabulated and agree closely with the values calculated from the equation  $P(104^\circ/0^\circ) = 12\cdot17 + 0\cdot3279t$ , the corresponding expression for rubidium chloride itself being  $P(115^\circ/0^\circ) = 44\cdot37 + 0\cdot1377t$ .

The double salt,  $4\text{RbCl}, \text{CdCl}_2$ , obtained from a solution of its components containing excess of the alkali chloride, separates in rhombohedral crystals the crystallographic examination of which indicates that the compound is isomorphous with the corresponding potassium derivative,  $4\text{KCl}, \text{CdCl}_2$ . It was not found possible to produce the double salts  $6(\text{CdCl}_2, \text{RbCl}), 3\text{H}_2\text{O}$  and  $4(\text{CdCl}_2, \text{RbCl}), \text{H}_2\text{O}$ , formerly described by Godeffroy (*Ber.*, 1875, 8, 9).

The solubility of the system  $4\text{RbCl}, \text{CdCl}_2 + \text{RbCl}, \text{CdCl}_2$  was studied, the results being tabulated and also expressed in the form of a curve. The transformation point of the double salt was not determined, however, owing to the fact that the system  $4\text{RbCl}, \text{CdCl}_2 + \text{RbCl}$  could not be obtained in solution, the double salt being practically insoluble

in rubidium chloride solution. This singular property of the double chloride is paralleled by the slight solubility of rubidium alum and rubidium magnesium chloride in solutions of aluminium salts and magnesium chloride respectively.

G. T. M.

**Determination of the Molecular Weights of Substances in the Liquid State.** By WLADIMIR A. KISTIAKOWSKY (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 70—90).—The author arrives at the following simplified formula for calculating the molecular weight of a liquid from the coefficient of capillarity:  $M = (2.3T/g.h.r.\rho^{1/3})^{3/2}$ , where  $T$  is the absolute boiling point of the liquid;  $g$  the acceleration due to gravity;  $h$  the height of the liquid in the capillary;  $r$  the radius of the capillary; and  $\rho$  the density of the liquid. A simplified form of apparatus is sketched and described, and the results of a number of measurements tabulated.

T. H. P.

**Chemical Dynamics of Nickel Carbonyl.** By ALWIN MITTASCH (*Zeit. physikal. Chem.*, 1902, 40, 1—83).—The vapour pressure curve of the compound was determined, and also the pressure-temperature curve of the unsaturated vapour. The latter curve is normal, the vapour obeying the gas laws, but evidences of decomposition were obtained at temperatures above 50°. The decomposition and progress of the reversible reaction,  $\text{Ni(CO)}_4 \rightleftharpoons \text{Ni} + 4\text{CO}$ , could hence be followed by a manometric method, which was that adopted by the author. A full description of the apparatus and method is given, as well as of the various difficulties which occurred, and the precautions necessary to meet them. The reaction was proved to be reversible, the same end state of the system being obtained when it is attained from higher as when it is attained from lower temperatures, that is, when the reaction is proceeding as a formation or as a decomposition process. The equilibrium constant is given by  $c_1^4/c_2$ , where  $c_1$  and  $c_2$  are the concentrations of carbon monoxide and of nickel carbonyl respectively, and satisfactory agreement was obtained for this constant in each set of experiments, but, as would be expected, it varies with the nature of the nickel employed. Increase of pressure should considerably decrease the decomposition, and this was experimentally verified. For mean concentrations, the whole range of the decomposition curve lies within a comparatively small range of temperature, being negligible at 0° and practically complete at 120°; a number of equilibrium curves, composition against temperature, are given for varying concentrations. The effect of various kinds of nickel was examined; it was found that the finest powder had the greatest active mass, and hence gave the smallest value for the decomposition. Traces of air were found to have a very marked inhibiting effect on the reaction, this being, however, counteracted by small quantities of hydrogen sulphide, whilst small quantities of mercury have an accelerative action. From the variation of the reaction constant with temperature, values for the heat of formation are obtained varying from 23 to 32 cals., whereas that determined experimentally by the author was 43.36 cals.; in the calculation, however, the effect of temperature on the active mass of the nickel itself is neglected. The velocities of formation and decomposition were also investigated. It was found, as is indicated theoretically,

that the temperature coefficient of the decomposition velocity is greater than that of the formation velocity. The decomposition proceeds as a unimolecular reaction, but, contrary to expectation, the formation was found to be bimolecular and not quadrimolecular. This indicates that the formation proceeds in two stages, with probably the formation of an intermediate compound,  $\text{Ni}(\text{CO})_2$ . L. M. J.

**Heterogeneous Equilibrium between mixed Isomorphous Crystals of Hydrated Salts.** By GIUSEPPE BRUNI and WILHELM MEYERHOFFER (*Atti R. Accad. Lincei*, 1902, 11, i, 185—190. Compare Abstr., 1901, ii, 11).—The authors consider the equilibrium existing between two isomorphous salts which dissolve in water giving one or more hydrates, of which those of corresponding composition form isomorphous pairs. A solution of two such salts can only have four phases, namely, two kinds of mixed crystals, solution and vapour. The temperature of transformation curve will hence be continuous and may, of course, have one of three forms. By the application of the method used by Roozeboom (Abstr., 1900, ii, 132) for the study of the phenomena of congelation and transformation of binary mixtures, and also of Gibbs's theorem according to which at any temperature that system is stable for which the function  $\zeta$  has the smaller value, the authors arrive at the conclusion that that component which, added to the system, produces a rise in the temperature of transformation is contained by the more highly hydrated mixed crystals in greater proportion than by those poorer in water.

The treatment of more complex cases, in which, for example, one or both the hydrates can be formed only within certain limits of temperature, involves analogous considerations, but the transformation curves will then show multiple points. T. H. P.

**Equilibrium in the System: Sodium Carbonate, Ethyl Alcohol, and Water.** By C. H. KETNER (*Zeit. physikal. Chem.*, 1902, 39, 641—690).—The equilibrium in the binary system sodium carbonate and water was first investigated and the absence of hydrates other than those of the composition  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ , and  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  was verified (Andreae, Abstr., 1891, 781). Of the two heptahydrates, one is stable and known as  $7\beta$ , the other,  $7a$ , is throughout in the labile state. The following equilibrium points were determined:  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} - \text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ —solution at  $35.1^\circ$ , and  $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O} - \text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ —solution at  $31.85^\circ$ , the heptahydrate being only stable therefore over a range of about three degrees. The equilibrium in the ternary system was then investigated: representing the solid phases by  $Z_{10}$ ,  $Z_7$ , and  $Z_1$ , the aqueous and alcoholic liquid phases by  $L_w$  and  $L_a$ , and the vapour phase by  $D$ , the following results were obtained. At temperatures above  $34.6^\circ$ , two liquid phases may be in equilibrium with the monohydrate, that is, the system  $Z_1 + L_w + L_a + D$  exists and the composition of the liquid phases are represented by curves. At  $34.6^\circ$  a quintuple point is obtained, the heptahydrate being now also formed, the system hence being  $Z_7 + Z_1 + L_w + L_a + D$ , the reaction with temperature change being  $Z_7 + L_a \rightleftharpoons Z_1 + L_w$ . Between  $34.6^\circ$  and  $31.1^\circ$ , the liquids can only be in equilibrium with the heptahydrate, but at  $31.1^\circ$  the decahydrate is first obtained

and a second quintuple point results,  $Z_{10} + Z_7 + L_w + L_a + D$ . The analyses for the determination of the various quadruple curves meeting at the quintuple points are recorded and the variation of solubility by addition of alcohol is seen. Diagrams of the isothermals are given. At  $21.8^\circ$ , the isothermal consists of four parts representing the solutions in equilibrium with the three stable hydrates and the anhydrous salt, the points of intersection of the curves giving the equilibrium points for  $Z_{10}Z_7$ ,  $Z_7Z_1$ , and  $Z_1Z$ . At  $27.7^\circ$ , the solubility curve of  $Z_{10}$  is tangential to the binodal curve, so that above this temperature two liquid layers in equilibrium with  $Z_{10}$  may occur and the isothermals for  $28.2^\circ$  and  $29.7^\circ$  are given. When the temperature reaches  $31.1^\circ$ , the equilibrium point for  $Z_{10}Z_7$  falls on the binodal curve, so that above this temperature  $Z_7$  may be in equilibrium with two conjugate solutions. Similarly, above  $35.1^\circ$  the monohydrate occurs in equilibrium with  $L_w$  and  $L_a$ . A representation of the complete equilibrium surface is also added. The vapour pressure curve was also investigated for the quadruple curve,  $Z_1 + L_w + L_a + D$ . It was found that for certain alcoholic concentrations, namely, all above 2.2 per cent., the addition of sodium carbonate lowers the boiling point and hence increases the vapour pressure.

L. M. J.

**Physical Peculiarities of Solutions of Gases in Liquids.** By J. ALFRED WANKLYN (*Phil. Mag.*, 1902, [vi], 3, 346—348).—When carbon dioxide is separated from strong potash by a layer of water saturated with the gas, no absorption is apparent for many hours. The author regards this as proof that there is no motion of the  $\text{CO}_2$  molecules among the  $\text{H}_2\text{O}$  molecules; probably one  $\text{CO}_2$  molecule forms with many  $\text{H}_2\text{O}$  molecules one big compound molecule. J. C. P.

**Solubility of Ammonia in Salt Solutions, as Measured by its Partial Pressure. I.** By RICHARD ABEGB and H. RIESENFELD (*Zeit. physikal. Chem.*, 1902, 40, 84—108).—The partial pressure of a solution was found by allowing electrolytic gas to pass through the solution and then through an absorption cell containing a solution of hydrogen chloride; from the variation in conductivity of the latter, the quantity of ammonia and hence the partial pressure was determined. It was found that the partial pressure was proportional to the concentration for solutions examined, which were about 0.5 *N* and 1.0 *N*. The salts examined were those of the alkali metals, and in almost all cases the addition of salt causes an increase of the partial pressure of ammonia, this increase being proportional to the concentration of the salt; lithium salts are, however, exceptional. No noteworthy results are obtained if the concentrations are expressed per 100 grams of water instead of per litre. The salts may be divided into two groups, those giving a molecular increase of pressure less than 2.3 and those giving the molecular increase greater than 3.4. Those giving the lower value are those containing univalent anions. The following, however, gave the higher value: hydroxides, fluorides, borates, acetates, formates, chlorates, and iodates, the action being apparently additive. The higher value appears to be connected with the tendency to form hydrates, whilst hydrates do not exist in the case

of the salts for which the lower value is obtained. From the change of partial pressure, the solubility lowering can be calculated, and this is found to be in general agreement with the lowering of solubility of other substances. By the comparison of the lowering of solubility at different temperatures, indications of chemical action may be obtained, and evidences of such action appear to exist in some cases, notably the alkali chlorides (compare Gahl, Abstr., 1900, ii, 389). L. M. J.

**Nitriles as Solvents in Molecular Weight Determinations.** By LOUIS KAHLENBERG (*J. Physical Chem.*, 1902, 6, 45—49).—Using the values recently obtained for the latent heat of evaporation of benzonitrile (Luginin, Abstr., 1900, ii, 334; Kahlenberg, this vol., ii, 195), the author finds the molecular elevation of the boiling point for this solvent to be 48·67—a value considerably greater than that used by Werner (Abstr., 1898, ii, 214). The author has recalculated Werner's results for the solutes diphenylamine, mercuric chloride and iodide, and silver nitrate, and adds a series of his own determinations with the last named. The molecular weight found is high in every case (40 to 50 per cent. higher than the theoretical value), a result probably connected with the high boiling point of the solvent. The solutions of mercuric chloride and iodide and silver nitrate are fairly good electrolytes; that of diphenylamine is a non-electrolyte.

The molecular elevation of the boiling point of acetonitrile is found to be 14·39. In this solvent, naphthalene and diphenyl give values that are slightly higher, diphenylamine and silver nitrate values that are lower, than the normal molecular weight. The solutions of naphthalene, diphenyl, and diphenylamine are non-electrolytes; that of silver nitrate is a very good electrolyte. J. C. P.

**Inorganic Ferments.** By DOUGLAS MCINTOSH (*J. Physical Chem.*, 1902, 6, 15—44. Compare Bredig and Müller von Berneck, Abstr., 1900, ii, 213; Bredig and Ikeda, Abstr., 1901, ii, 441; Bredig and Reinders, Abstr., 1901, ii, 442).—The paper deals chiefly with the catalytic effect of colloidal silver on the decomposition of hydrogen peroxide, and the results are summarised as follows. In acid or neutral solution, colloidal silver decomposes hydrogen peroxide until it is dissolved; the rapid decomposition induced by colloidal silver in alkaline solution follows the course of a unimolecular reaction. Silver salts in alkaline solution are completely reduced to silver, which then exerts the same catalytic influence as colloidal silver. Substances which form compounds with silver not decomposed by hydrogen peroxide exert a retarding influence on the catalysis. Colloidal mercury, or mercury reduced from its salts, acts in alkaline solution like colloidal silver. J. C. P.

**Solutions of Inorganic Salts in Water.** By WILHELM BILTZ [with JULIUS MEYER] (*Zeit physikal. Chem.*, 1902, 40, 185—221).—It is recognised that a number of electrolytes do not give values for the degree of dissociation in agreement with Ostwald's dilution law; but the number is not great and the authors believe that more details must be obtained before the reason for the deviations can be arrived



at. In order to contribute to this subject, the authors have determined the cryoscopic values of several salts in aqueous solution over a wider range of concentration than has yet been done.

The vapour pressure of solutions of the chlorides of calcium, strontium, and barium was determined at 25° by the method described by Walker (Abstr., 1889, 6). The molecular weights calculated from the results show no progressive change, indicating that there is no retrogression of the dissociation with increasing concentration up to 100 grams per litre of water.

The cryoscopic behaviour of solutions of the following salts was determined in a specially constructed apparatus: chlorides of caesium, rubidium, potassium, ammonium, sodium, lithium, mercury, copper, zinc, manganese, nickel, cobalt, and iron ( $\text{FeCl}_2$ ); bromides of aluminium and copper; potassium thiocyanate, cyanide, bromide, iodide, and fluoride; and lithium nitrate, bromide, and iodide. The solutions examined varied from 0.04*N* to 0.6*N*, and the results are given graphically, using the normalities as abscissæ, and the corresponding molecular depressions of the freezing point, *k*, as ordinates. The curves obtained for the chlorides of the alkali metals show that when the metals are arranged according to the magnitude of the deviation from the law of mass action we obtain the series: Cs, Rb, K,  $\text{NH}_4$ , Na, Li. In the same way, the following series is obtained from the chlorides of bivalent metals: Ba, Sr, Cu, Zn, Mn, Ca, Ni, Co, Mg, Fe. In all these cases, *k* exhibits a minimum value. The values obtained for mercuric chloride confirm the observation that this is very little dissociated. For aluminium bromide, the values of *k* varied from 14 to 10.7, when the concentration changed from 0.078*N* to 4.355*N*, and this leads to the conclusion that in aqueous solution aluminium bromide exists in double molecules at high concentrations. From the results with the potassium and lithium salts, it is seen that the order in which the anions affect the deviation is: SCN, CN, Cl, Br, F, I the last having the greatest effect.

Ebullioscopic determinations have been made with the chlorides of some of the alkali metals, and the results are in fair agreement with the cryoscopic values for the molecular weight.

The results obtained show that when the salts are arranged according to the *k* values the same series is arrived at as when they are ordered according to their molecular heats of solution.

The degrees of dissociation of rubidium and caesium nitrates have been calculated, and it is found that the change is not regular. The same is true of the degrees of dissociation of these two salts as found from the conductivity of the solutions.

The series given above for the cations and anions is the same as their decomposition tensions and the author connects this with Abegg and Bodländer's theory (Abstr., 1899, ii, 542), and assumes that complex formation takes place, water being the neutral component. The deviations can be accounted for by assuming that hydrates are formed in solution. Tentatively, it is calculated that in 0.1 to 0.5 *N* solution potassium and sodium chlorides near 0° chemically bind about 40 mols. of water per mol. of salt. The complexes are broken down as the temperature rises, and therefore we should expect results from

ebullioscopic determinations would give values in closer agreement with the law of mass action than those obtained at  $0^{\circ}$ ; as Kahlenberg (*J. Physical Chem.*, 1901, 5, 375) has recently shown, this is probably the case. Formation of hydrates is also shown to be supported by the heats of solution. J. McC.

**Properties of Nitrogen Peroxide as a Solvent.** By GIUSEPPE BRUNI (*Gazzetta*, 1902, 34, i, 187—188).—A claim for priority (see Abstr., 1900, ii, 591; *Proc.*, 1902, 47). T. H. P.

**Gelatinisation.** By S. A. LEVITES (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 110—118).—The author has examined the gelatinisation of gluten,  $\delta$ -galactan and starch under various conditions, more especially in the presence of certain salts, which exert a retarding influence on the gelatinisation. The temperature at which starch forms a paste is lowered by the presence of salts; the following table gives the temperatures of gelatinisation for maize starch which ordinarily forms a paste at  $66$ — $68^{\circ}$ :

In 10 per cent. ammonium or potassium thiocyanate ...	46—48°
„ 20 „ potassium or sodium iodide .....	46—48
„ 20 „ „ „ bromide .....	52—54
„ 20 „ ammonium nitrate .....	52—54

In a solution containing 15—20 per cent. of ammonium or potassium thiocyanate, or 40 per cent. of potassium or sodium iodide or 50—60 per cent. of the bromide, maize starch gelatinises at the ordinary temperature. Zulkowski's starch solution, which contains 10—20 parts of starch per 100 of water and solidifies to a stiff jelly, is entirely prevented from gelatinising by the presence of 10 per cent. or even less of potassium or sodium iodide or thiocyanate. Other substances such, for instance, as di- and tri-hydric phenols, exert an influence on the gelatinisation of these substances similar to those of salts.

From the results of his measurements, the author supposes that such retardation of the process of gelatinisation is due to the more ready solubility of the gelatinising substances in the salt solutions; and the greater this solubility the more slowly will the gelatinisation take place. Analogies are indicated between the separation of crystalline compounds from solution and the gelatinisation of colloids.

T. H. P.

**Position of the Rare-Earth Elements in Mendeléeff's Periodic System.** By BOHUSLAV BRAUNER (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 142—153).—After considering the properties of, and the compounds formed by, the metals of the rare-earths, the author proposes an alteration in Mendeléeff's table by which the elements Ce, Pr, Nd, Sa, En, Gd, Tb, Ho, Er, Tu, Yb are placed in an inter-periodic group. T. H. P.

**New Flasks for Washing and Drying Gases.** By WETSCHIAS-LAW E. TISTSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 67—79).—The

author describes, with sketches, a new form of washing apparatus for gases. It consists of a cylindrical glass vessel standing on a foot and divided into two halves by a vertical partition passing down the middle. If the washing material is solid, this partition terminates some distance from the bottom, whilst if the apparatus is to contain liquid, the partition passes the whole way down except for a small distance in the middle, where a small opening is left for the gas to bubble through from one side to the other. Two tubes, one in each half of the vessel, serve as inlet and outlet tubes and an aperture, closed by a stopper, in the top allows of the charging and cleaning out of the apparatus. The stream of gas passes from the top to the bottom of one side of the vessel, then under the partition, up the other side, and out by means of the exit tube. The device is simple, effective, and not readily broken.

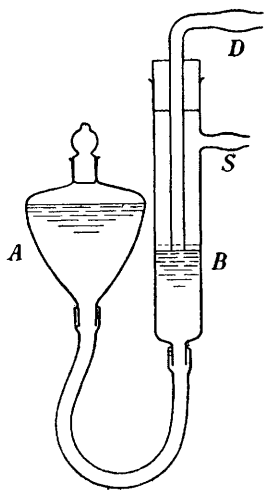
T. H. P.

**Pressure Regulator for Vacuum Distillation in the Laboratory.** By WALTER BURSTYN (*Chem. Centr.*, 1902, i, 614—615; from *Oesterr. Chem. Zeit.*, 5, 55—56).—By means of the apparatus or "manostat," shown in the figure, the pressure in the distilling flask during distillation under diminished pressure may be automatically kept within certain limits.

The glass vessels *A* and *B* are connected by pressure tubing and filled with mercury to the levels shown in the figure. The air-pump and distilling apparatus are connected with *S* and *D* respectively. Before the pump is set going, the vessel *A* is completely filled with mercury by lowering it and then carefully inserting the stopper. The air is then pumped out, and as soon as the pressure is reduced to the required amount (for example, 20 mm.), *A* is raised until the mercury in *B* just touches the lower end of the tube *D*, a Torricellian vacuum being formed in *A*. If the pressure then sinks below the required amount (for example, to 15 mm.), the difference is at once equalised by the rising of the mercury in *B* (5 mm. to the dotted line). When the pressure is increased by the entry of air or liberation of gas, the excess is removed by the pump. With this arrangement it is not necessary to use a pressure flask, but the volume of connecting tubes, &c., between the manostat and the pump should be reduced to a minimum.

In cases where a mercury pump is used and a vacuum of 5 mm. or less is required, it is better to fill the manostat with paraffin oil, which is only one-fifteenth as heavy as mercury; the vapour tension of the paraffin oil need not be considered.

E. W. W.



## Inorganic Chemistry.

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**Decomposition of Hydrogen Peroxide by Various Substances at High Temperatures.** By J. H. KASTLE and MARY E. CLARKE (*Amer. Chem. J.*, 1901, 23, 518—526).—The amount of oxygen liberated from hydrogen peroxide solution at 100° in presence of various salts was determined. Iron salts, potassium iodide, and chrome alum decompose the hydrogen peroxide with great rapidity; with nickel and cobalt salts, the decomposition is much slower, but ultimately it is very nearly as great. Other salts cause a much more gradual decomposition. In the case of certain salts, notably copper sulphate and potassium dichromate, the decomposition seems to be a true catalysis. The most active substances appear to be those which are acted on chemically by the hydrogen peroxide or those containing an element capable of combining with oxygen in several different proportions. The investigation is being continued. J. McC.

**Behaviour of Hydrogen Peroxide with certain Salts.** By PETR G. MELIKOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 207—210).—The compounds obtained by the action of hydrogen peroxide on various salts are of three kinds: (1) compounds of per-acids with hydrates of metallic oxides; (2) compounds of normal acids with metallic peroxides; (3) compounds of per-acids with metallic peroxides. From a consideration of the work described by Kazanezky and by Petrenko, and of his own work with Pissarjewsky (this vol., ii, 316, 317, 326), the author draws the following conclusions. The elements of the fourth group having high atomic weights yield per-acids with hydrogen peroxide; this is also the case with the element boron of low atomic weight, the oxide of which has both basic and acid properties. Elements with acid properties only yield per-acids by means of the electrolysis of their salts. T. H. P.

**Relative Strength of Hydrochloric and Nitric Acids.** By G. BODLÄNDER and OTTO SACKUR (*Ber.*, 1902, 35, 1255).—A reply to Kühling (this vol., ii, 252). W. A. D.

**Pure Iodine.** By ALBERT LADENBURG (*Ber.*, 1902, 35, 1256—1257).—"Pure" potassium iodide was converted into silver iodide and the latter freed from silver chloride by shaking for 24 hours with concentrated ammonia; the ratio of the solubility in ammonia of silver iodide to that of silver chloride is approximately 1:1000, and the silver iodide as treated above, was considered pure when its solubility in 100 parts of ammonia of sp. gr. 0.971 reached a constant value of 0.0045. Pure iodine was obtained by reducing the silver iodide with zinc and sulphuric acid, precipitating the solution with nitrous acid, distilling with steam, and drying over calcium chloride; it was blacker and less volatile than ordinary iodine, boiled at 183.05° (corr.), melted in a Roth's apparatus at 116.1° and had a sp. gr. 4.933 at 4°/4°. W. A. D.

**Double Salts of Iodine Trichloride with Chlorides of Divalent Metals.** By RUDOLPH F. WEINLAND and FR. SCHLEGELMILCH (*Zeit. anorg. Chem.*, 1902, 30, 134—143).—The double salts were prepared by adding excess of iodine to a saturated solution of the metallic chloride and passing a current of chlorine through the solution; on cooling, the double salt separates out and is dried on porous porcelain. They all crystallise well, but are very unstable and hygroscopic; carbon tetrachloride extracts iodine trichloride from them. They all have the formula  $2\text{ICl}_3 \cdot \text{MCl}_2 \cdot 8\text{H}_2\text{O}$ . The following have been obtained: *cobalt* salt, dark orange-red needles; *Nickel* salt, fine green crystals; *manganese* salt, orange-red needles; *zinc* salt, golden plates; *beryllium* salt, yellow needles; *magnesium* salt, yellow needles; *calcium* salt, golden needles, and *strontium* salt, golden needles. It has not been possible to obtain double salts with the chlorides of barium, cadmium, copper, mercury, or lead. J. McC.

**The Existence of a Blue or Green Modification of Sulphur.** By N. A. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 52—67. Compare Abstr., 1901, ii, 499).—From a consideration of the work previously published on this subject and of his own experiments, the author concludes that there exists a peculiar modification of sulphur, which has a blue or (when mixed with the yellow form?) green colour and is very unstable, being only able to exist (1) at the moment of its formation in certain reactions and in a peculiar state of fixation on some chlorides, and (2) more stably combined with certain inorganic, and possibly also organic, compounds. Among the conditions of formation of this modification of sulphur, the most striking is the influence of dissociation or of the incompleteness of the reactions yielding it. Such reactions are that of ammonium monosulphide with alcohol or acetone, or that obtained on heating potassium thiocyanate to redness, yielding the cyanate and sulphur. Nothing definite is known concerning the molecular structure of blue sulphur, but there are indications that the molecule is analogous to that of ozone and has the formula  $\text{S}_3$ ; the resemblance to ozone is also shown in the difficulty of preparation.

T. H. P.

**Theory and Practice of the Lead Chamber Process.** By GEORG LUNGE (*Zeit. angew. Chem.*, 1902, 15, 145—154).—In the present paper, the author criticises more especially the recent publications of T. Meyer (*ibid.*, 1901, 14, 1245) and of E. Loew (*ibid.*, 1900, 13, 338), as well as former attempts made by Hurter to apply the law of mass action to the reactions in the lead chamber. Such attempts have failed, to a large extent at least, for the reason that the reactions are not so simple as have been assumed, and also because the experimental investigation is as yet insufficient to supply the necessary ground-work on which to base the mathematical treatment. Moreover, mistakes have been made owing to insufficient acquaintance with the law of mass action and to disregard of intermediate reactions. The author restates his view that the reactions in the lead chambers consist first in the formation of nitrosylsulphonic acid, and that the latter is then decomposed by water into nitrous and sulphuric acids;

the former decomposes into water and oxides of nitrogen, which again form nitrosylsulphonic acid with sulphur dioxide. To the first reaction, the law of mass action cannot be applied, but the second, which is reversible, is susceptible of such treatment, and it should be possible to calculate the best conditions with regard to temperature and amount of water. The author also criticises the practical suggestions made by Meyer, and cannot see that they possess many advantages over the methods already existing.

A. F.

**Tellurium Tetrachloride.** By VICTOR LENHER (*J. Amer. Chem. Soc.*, 1902, **24**, 188—190).—If tellurium is treated with excess of sulphur monochloride at the ordinary temperature, tellurium tetrachloride is produced; it may be purified by washing with carbon disulphide. When the vapour of sulphur monochloride is passed over strongly heated tellurium, the black tellurium dichloride is first formed, but rapidly changes into the tetrachloride, which is deposited in long needles on the cool parts of the tube.

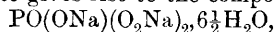
E. G.

**Ionic and Thermal Coefficients of Nitric Acid.** By VICTOR H. VELEY and J. J. MANLEY (*Phil. Mag.*, 1902, [vi], **3**, 118—122).—From their previous determinations of the conductivity of nitric acid (Abstr., 1898, ii, 277), the authors have calculated the values of  $\mu/\mu_{\infty}$  at 15° for acid of 1.3 to 99.97 per cent. concentration. It is probable that the change in the temperature coefficient of conductivity at 96 per cent. concentration (*loc. cit.*) is connected with the formation of the compound  $2\text{HNO}_3 \cdot \text{N}_2\text{O}_5$ .

From their determinations of the density of nitric acid at different temperatures (Abstr., 1901, ii, 447), the authors have calculated the coefficient of thermal expansion. The coefficient increases with the concentration to  $1274 \times 10^{-6}$  for the 100 per cent. acid (temperature range 4—14°), a value 27 times as great as that of water. If the coefficients of thermal expansion are plotted against percentage composition, the resulting points lie approximately on four straight lines—firstly, from 1 to 8 per cent. ; secondly, from 11 to 54 per cent. ; thirdly, from 54 to 70 per cent. ; fourthly, from 70 to 93 per cent. ; the remainder lie on an irregular curve: it is noted that 54 per cent. is also the point of maximum contraction.

J. C. P.

**Action of Hydrogen Peroxide on Phosphates.** By G. I. PETRENKO (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 204—207).—When acted on by hydrogen peroxide, phosphoric acid does not yield a corresponding per-acid, but its salts give compounds in which the metal is partially replaced by the residue of a metallic peroxide. Thus, sodium phosphate gives rise to the compound



which is readily decomposed by water with formation of hydrogen peroxide. It is probable that ammonium phosphate forms a similarly constituted compound, but this could not be isolated owing to the readiness with which it loses ammonia and oxygen; compounds were separated in which the ratio P:O:NH<sub>3</sub> had the values 5:8:14 and 2:3:5.

T. H. P.

**Hydrazine Borates.** By A. DJAVACHOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 227—230).—When boric acid solution is neutralised with hydrazine hydrate and the liquid evaporated partially on the water-bath and afterwards left in a desiccator over sulphuric acid, rhombic crystals are deposited which have the composition  $(\text{N}_2\text{H}_4)_2(\text{H}_2\text{B}_4\text{O}_7)_3 \cdot 10\text{H}_2\text{O}$ , and rapidly effloresce in the air. When kept in a vacuum over sulphuric acid until they attain a constant weight, these crystals lose water, the final composition being  $(\text{N}_2\text{H}_4)_2(\text{H}_2\text{B}_4\text{O}_7)_3 \cdot 5\text{H}_2\text{O}$ . On heating at  $100^\circ$ , the remaining  $5\text{H}_2\text{O}$  are given up, whilst at  $250$ — $260^\circ$  the compound assumes the composition  $(\text{N}_2\text{H}_4)_2(\text{B}_2\text{O}_3)_6$ . When heated above  $260^\circ$ , the last substance melts and is decomposed into hydrazine and boric oxide. Attempts to prepare crystalline borates of hydrazine other than the above have failed.

T. H. P.

**Derivatives of Perboric Acid.** By G. I. PETRENKO (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 37—42).—The action of hydrogen peroxide on potassium fluoroborate yields a potassium fluoroperborate of the constitution,  $\text{K} \cdot \text{O} \cdot \text{O} \cdot \text{BF} \cdot \text{O} \cdot \text{O} \cdot \text{BF} \cdot \text{O} \cdot \text{K}$ ; with ammonium fluoroborate, the corresponding ammonium fluoroperborate is obtained together with ammonium perborate. Ammonium peroxide acts as a base towards perboric acid, with which it combines, giving a salt-like compound.

T. H. P.

**Direct Hydrogenation of the Oxides of Carbon in the Presence of various finely-divided Metals.** By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1902, 134, 689—691. Compare this vol., i, 333).—Although carbon monoxide is completely converted into methane by hydrogen in the presence of finely-divided nickel (*loc. cit.*) at  $250^\circ$ , at  $280^\circ$  another reaction becomes at the same time obvious, namely, the formation of carbon dioxide and very finely-divided carbon. Thus at  $380^\circ$ , carbon monoxide (1 vol.) and hydrogen (3 vols.) yield a gaseous mixture, which consists of carbon dioxide 10.5, methane 67.9, and hydrogen 21.6 per cent.; whilst when equal volumes of carbon monoxide and hydrogen (water gas) are used, 52.5 per cent. of carbon dioxide, 39.8 of methane, 7.1 of hydrogen, and 0.6 per cent. of carbon monoxide are formed.

Cobalt resembles nickel in its action on mixtures of carbon dioxide and hydrogen or carbon monoxide and hydrogen, but is less energetic; the reduction of carbon dioxide begins at  $300^\circ$  and is rapid at  $360$ — $400^\circ$ ; no formation of carbon or carbon monoxide, and no oxidation of the metal occurs. Carbon monoxide begins to be reduced at  $270^\circ$ , but at  $300^\circ$  the formation of carbon dioxide and carbon is also noticeable; the latter reaction plays a more prominent part the higher the temperature and the greater the proportion of carbon monoxide in the mixture of this gas and hydrogen, which is led over the cobalt. Platinum sponge and platinum black, palladium sponge and reduced iron, do not bring about the reduction of the oxides of carbon. Reduced copper converts a mixture of hydrogen and carbon dioxide into carbon monoxide and water at  $430^\circ$ .

K. J. P. O.

**Action of Hydrogen Peroxide on Carbonates.** By P. KAZANEZKY (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 202—204).—Five grams

of freshly-prepared ammonium carbonate were dissolved in 40 c.c. of 20 per cent. hydrogen peroxide, and the solution, after cooling in ice, mixed with 5 c.c. of aqueous ammonia saturated at 0°. The addition to the liquid of 2—3 vols. of alcohol then gave a white, crystalline precipitate of a salt having the constitution  $\text{NH}_4 \cdot \text{O} \cdot \text{O} \cdot \text{CO} \cdot \text{O} \cdot \text{NH}_4, 2\text{H}_2\text{O}$ . The salt is readily soluble in water, by which it is almost completely decomposed into hydrogen peroxide and ammonium carbonate.

T. H. P.

**New Silicon Hydride.** By HENRI MOISSAN and S. SMILES (*Compt. rend.*, 1902, 134, 569—575).—The action of hydrochloric acid on the mixture of magnesium silicides obtained by heating magnesium and silicon together in the proportions Si : Mg<sub>2</sub>, yields hydrogen containing about 5 per cent. of silicon hydrides. If this mixture is passed through tubes cooled by liquid air or oxygen, the silicon hydrides solidify, and by allowing the solid to liquefy and volatilise fractionally the hydride Si<sub>5</sub>H<sub>6</sub> is obtained as a mobile, colourless liquid which boils at about 52°, takes fire spontaneously at the ordinary temperature, and burns brilliantly and even explosively, and is decomposed completely at about 250°. When solidified by means of liquid air, it melts at -138°. It is attacked by potassium hydroxide solution with liberation of hydrogen and formation of an alkali silicate, and it reduces solutions of mercuric chloride, auric chloride, and silver nitrate.

C. H. B.

**Solubility of Potassium Hydroxide in Water.** By P. FERCHLAND (*Zeit. anorg. Chem.*, 1902, 30, 130—133).—The concentration of a saturated solution of potassium hydroxide, prepared from electrolytic potassium amalgam, was found to be 51.76 per cent. at 15.8°, and 51.72 per cent. at 15°. The sp. gr. of the solution at 15° is 1.5355. One hundred parts of water dissolve 107 parts of potassium hydroxide. This result agrees with that of Pickering (*Abstr.*, 1894, ii, 308).

J. McC.

**New Sodium Phosphate.** By H. JOULIE (*Compt. rend.*, 1902, 134, 604—606).—When disodium phosphate is mixed with sufficient phosphoric acid solution of sp. gr. 1.35 to make it neutral to litmus, complete dissolution takes place and the temperature falls to -13°. If the liquid product is concentrated until a pellicle forms and is then heated at 45—50° for some time, it gradually deposits colourless, oblique prisms of sodium sesquiphosphate,  $\text{Na}_3\text{H}_3(\text{PO}_4)_2$ , which is not hygroscopic, but dissolves in water in all proportions. It is neutral to litmus, has a slightly saline taste, and by reason of its high solubility may form an advantageous means of administering phosphoric acid.

C. H. B.

**An Acid Monosodium Orthophosphate.** By H. GIRAU (*Compt. rend.*, 1902, 134, 711—713).—The crystals which frequently appear on the outside of the sticks of commercial metaphosphoric acid are shown to have the composition  $\text{NaH}_2\text{PO}_4, \text{H}_3\text{PO}_4$ ; this very deliquescent substance is a definite salt, as its heat of dissolution in water, 1.12 Calories, differs from the heat of dissolution of a mixture of phosphoric acid and sodium dihydrogen phosphate, which amounts to 2.56 Calories (calculated). As commercial metaphosphoric acid has



approximately the composition  $\text{NaPO}_3, \text{HPO}_3$ , the above-mentioned salt appears to be formed by the fixation of two mols. of water. It is suggested that the salt described by Joulie (preceding abstract) is represented by the formula  $\text{Na}_3\text{PO}_4, \text{H}_3\text{PO}_4$ . K. J. P. O.

**Sesquisodium Phosphate.** By JEAN B. SENDERENS (*Compt. rend.*, 1902, 134, 713—714. Compare preceding abstracts).—It is pointed out that the salt  $\text{Na}_3\text{PO}_4, \text{H}_3\text{PO}_4$  described by Joulie is merely the anhydrous form of a salt previously described by the author (*Abstr.*, 1882, 693), which, when air-dried, crystallises with  $15\text{H}_2\text{O}$ ; it loses  $12\text{H}_2\text{O}$  in an exhausted desiccator over sulphuric acid, and becomes anhydrous at  $110^\circ$ . K. J. P. O.

**Reactions occurring in Solutions employed for the combined Toning and Fixing of Prints on Silver Chloride-Citrate Paper and the Theory of this Operation.** By AUGUSTE LUMIERE, LOUIS LUMIERE and ALPHONSE SEYEWETZ (*Bull. Soc. Chim.*, 1902, [iii], 27, 137—153).—Employing Lumière's combined toning and fixing mixture, consisting of sodium thiosulphate, alum, lead acetate, and gold chloride, the authors have studied the different reactions which take place on dissolving that mixture in water, as well as the action which these substances and the products of their interaction have on the photographic image on silver chloride-citrate paper. On preparing the mixed solution of the four salts mentioned, a complex series of reactions occur, there being produced, together with other substances, aluminium sulphate and sodium hydrogen sulphite, sodium pentathionate, and hydrogen sulphide. From their study of the action of the different substances on the photographic image, the authors chiefly conclude that the lead, present as the double sodium lead thiosulphate, accelerates the replacement of silver in the print by gold. The place of lead in this case may be taken by other metals, although with less satisfactory results. Lead does not enter into the composition of the toned image. The chief value of the alum, besides its tanning action, appears to be that of giving rise to pentathionic acid with sodium thiosulphate, and it is shown that the addition of that acid or of its lead salt produces a more active toning bath. Excess of acid added to the toning and fixing bath in absence of lead produces as rapid toning as when lead is present, this effect being probably due to the formation of pentathionic acid. With a solution containing lead pentathionate but no gold, as fine tones can be produced as when gold is present.

A. F.

**Polyhalogen Compounds of the Alkaline Earth Metals.** By JULIUS MEYER (*Zeit. anorg. Chem.*, 1902, 30, 113—121).—The solubility of iodine in solutions of the alkaline earth haloids has been determined. One hundred c.c. of a 10 per cent. solution dissolve the following quantities of iodine (in grams):

	$\text{Cl}_2$	$\text{Br}_2$	$\text{I}_2$
Ba .....	0·067	0·231	6·541
Sr.....	0·066	0·270	6·616
Ca .....	0·078	3·274	8·062
Temp. ....	$18\cdot5^\circ$	$13\cdot5^\circ$	$13\cdot5^\circ$

To decide whether the extra quantity of iodine was simply dissolved or chemically united, a cryoscopic method was used. Addition of iodine to a solution of barium iodide hardly depresses the freezing point, and the results are in agreement with the assumption that barium tetraiodide exists in the solution. Similar results were obtained with calcium and strontium iodides. These polyhalogen compounds are highly dissociated.

Calcium tetraiodide can be prepared by mixing calcium iodide and iodine (in mol. proportion) and warming on a water-bath. Between  $70^{\circ}$  and  $80^{\circ}$  the mixture melts, and on cooling a homogeneous, crystalline mass separates. Carbon disulphide or chloroform extracts two atoms of iodine. Barium and strontium tetraiodides can be prepared in the same way, but they are not so stable.

Crystalline masses the composition of which is represented by  $MI_6$ ,  $MI_8$ , and  $MI_{10}$  can also be obtained, but on dissolving them in water, iodine is separated with formation of tetraiodide. It has not been possible to isolate a tetrabromide.

The tetraiodides exist as such in solution, but the solids are best regarded as molecular compounds of  $MI_2$  and  $I_2$ . J. McC.

**Ammonium Calcium Phosphate.** By HENRI LASNE (*Bull. Soc. Chim.*, 1902, [iii], 27, 131—135).—The author confirms Barthe's statement (Abstr., 1900, ii, 480) as to the non-existence of the ammonium barium phosphate described by Kippenberger. He shows, however, that ammonium calcium phosphate can be prepared by the action of ammonium phosphate on calcium chloride in presence of a sufficient quantity of ammonium citrate to prevent the precipitation of calcium phosphate from the ammoniacal solution. Too great a concentration of ammonia and of ammonium phosphate must be avoided. The salt is crystalline, and has the composition  $CaNH_4PO_4 \cdot 7H_2O$ . It is decomposed by cold water with formation of tricalcium phosphate and triammonium phosphate, but when heated with water other products appear also to be formed. A. F.

**Solubility of Calcium Carbonate in Aqueous Solutions of certain Electrolytes in Equilibrium with Atmospheric Air.** By FRANK K. CAMERON and ATHERTON SEIDELL (*J. Physical Chem.*, 1902, 6, 50—56. Compare Cameron and Briggs, this vol., ii, 64; Cameron, this vol., ii, 75; Cameron and Seidell, this vol., ii, 207).—The solubility curve of calcium carbonate in sodium chloride solution, in equilibrium with ordinary air, shows a maximum; the solutions contain no normal carbonates. Sodium sulphate markedly increases the solubility of calcium carbonate, and the resulting solutions contain both acid and normal carbonate; the solubility of the calcium carbonate increases with increasing concentration of sodium sulphate up to the point of saturation of the latter. The solubility curve of calcium carbonate in sodium chloride solutions, calcium sulphate being present in the solid phase, shows a break; in equilibrium with ordinary air, the solutions contain no normal carbonates. J. C. P.

**Calcium Silicide,  $CaSi_2$ .** By HENRI MOISSAN and W. DILTHEY (*Compt. rend.*, 1902, 134, 503—507; *Ber.*, 1902, 35, 1106—1110).—Calcium silicide was prepared by fusing calcium oxide with excess of

silicon in a carbon tube in an electric furnace; the fused mass consisted of calcium carbide and calcium silicate surrounding a nucleus of the silicide, generally containing a variable quantity of silicon. The silicide forms brilliant greyish, brittle crystals, having a sp. gr. 2.5; it takes fire in fluorine at the ordinary temperature, forming calcium fluoride and silicon fluoride; when heated to dull redness in chlorine, bromine, or iodine, it becomes incandescent, yielding the calcium and silicon haloids. When heated in air, the silicide is only superficially attacked, but in oxygen it burns, forming calcium oxide and silica. Sulphur and hydrogen sulphide attack it very superficially. When heated with carbon in the electric furnace, calcium and silicon carbides are formed. Fused copper does not dissolve the silicide; fused aluminium decomposes it, producing aluminium silicide; fused iron behaves similarly.

Water decomposes the silicide very slowly, giving silica and pure hydrogen. Concentrated sulphuric acid dissolves it with slight evolution of hydrogen. Dilute nitric acid attacks it slowly, forming silicon and evolving hydrogen. In hydrogen fluoride, the silicide becomes incandescent. Hydrogen chloride does not attack the silicide at the ordinary temperature, but at a red heat decomposes it with incandescence, forming the chlorides of silicon and calcium. Concentrated cold hydrochloric acid produces hydrogen, silicon hydride, and silicon, whilst the dilute acid gives with the silicide, hydrogen and a yellow substance. Solutions of alkalis very readily dissolve calcium silicide with the evolution of hydrogen.

K. J. P. O.

**Formation of Oceanic Salt Deposits, particularly of the Stassfurt Beds. XXV. Formation of Langbeinite and its Lower Temperature Limits in the Salt Deposition at 37°.** By JACOBUS H. VAN'T HOFF, WILHELM MEYERHOFFER, and F. G. COTTERELL (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 276—282).—Langbeinite,  $K_2Mg_2(SO_4)_3$ , occurs in the polyhalite regions at Wilhelmshall and accompanies sylvite at Westeregeln. The most suitable langbeinite for dilatometric experiments is that obtained in the wet way, and this can best be prepared from magnesium and potassium sulphates and magnesium chloride by digestion on the water-bath.

Its formation from blödite,  $K_2Mg(SO_4)_2 \cdot 4H_2O$ , takes place at 89° as has been found by the dilatometer, and this was confirmed by observing the characteristic tetrahedral crystals when blödite was stirred in its saturated solution at 90°.

Presence of magnesium sulphate hexahydrate depresses the temperature of formation from blödite, and langbeinite is produced at 61°. This temperature may, however, be easily passed without the change taking place, and then at 72° the compound  $K_2Mg_4(SO_4)_5 \cdot 5H_2O$  (Abstr., 1900, ii, 284) is formed; this compound is unstable, for when langbeinite is added it is slowly converted into this.

In presence of sodium chloride, the temperature of formation may be still further depressed. The naturally accompanying minerals are magnesium sulphate hexahydrate, kainite, blödite, and sylvite, and it has

been proved that from a mixture of these langbeinite is formed at about 37°. Its occurrence along with sylvite indicates that it has been formed at a higher temperature than this. J. McC.

**Action of Hydrogen Peroxide on Zinc Oxide.** By ROBERT DE FORCRAND (*Compt. rend.*, 1902, 134, 601—604).—When zinc oxide is agitated for a long time with an excess of hydrogen peroxide, a *zinc peroxide*,  $\text{Zn}_4\text{O}_7$ , is obtained which is stable at the ordinary temperature and when dried approximates closely to the composition  $\text{Zn}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ . This represents the limit of oxidation under the conditions indicated, but if the partially dried product containing not less than 4.5 and not much more than 5  $\text{H}_2\text{O}$  is treated with a fresh quantity of hydrogen peroxide, a product is obtained which approximates closely to  $\text{ZnO}_2$ , but is unstable even at the ordinary temperature. When the hydrated oxide,  $\text{Zn}_4\text{O}_7$ , is heated at 100°, it yields the oxide,  $\text{Zn}_3\text{O}_5 \cdot 3\text{H}_2\text{O}$ , already known. There is no evidence of the existence of an oxide between  $\text{ZnO}$  and  $\text{Zn}_3\text{O}_5$ , and the products obtained by Thenard and by Kouriloff seem to have been mixtures of the monoxide with one or more of the higher oxides,  $\text{Zn}_3\text{O}_5$ ,  $\text{Zn}_4\text{O}_7$ , or  $\text{ZnO}_2$ .

C. H. B.

**Electrolytic Production of Lead Dioxide.** CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P 124512).—Lead dioxide is conveniently prepared by electrolysing a solution of an alkali chloride in which litharge is suspended. The dioxide is formed by the action of nascent chlorine and sodium hypochlorite on the soluble sodium plumbite, produced from the monoxide and the sodium hydroxide set free at the cathode, the reactions taking place in accordance with the following equations:  $\text{Pb}(\text{ONa})_2 + \text{NaOCl} + \text{H}_2\text{O} = \text{PbO}_2 + 2\text{NaOH} + \text{NaCl}$  and  $\text{Pb}(\text{ONa})_2 + 2\text{Cl} = \text{PbO}_2 + 2\text{NaCl}$ . Hydrogen is steadily evolved at the cathode, but there is no loss of chlorine at the anode. G. T. M.

**Compounds of Thallium.** By VICTOR THOMAS (*Compt. rend.*, 1902, 134, 545—547. Compare Cushman, *Amer. Chem. J.*, 1901, 26, 505).—Thallic chloride,  $\text{TlCl}_3$ , is quite stable in dilute solutions in presence of hydrochloric acid. Thallous chloride and bromine yield a *compound*,  $\text{TlClBr}_2 \cdot 4\text{H}_2\text{O}$  (?); on attempting to dehydrate this salt, the compound  $\text{Tl}_3\text{Cl}_2\text{Br}_4$  is always produced. Chlorine and thallous bromide give a *compound*,  $\text{TlCl}_2\text{Br} \cdot 4\text{H}_2\text{O}$ . Thallous bromide, suspended in water and treated with bromine, yields thallic bromide,  $\text{TlBr}_3 \cdot 4\text{H}_2\text{O}$ , crystallising in large, prismatic needles, which lose bromine readily with the formation of the dibromide. All these thallic halogen compounds form compounds with the halogen acids of the type,  $\text{TlX}_3 \cdot \text{HX}$ , which are extremely soluble in water and have not yet been obtained in a solid state. K. J. P. O.

**Some Complex Compounds of Thallium, and the Constitution of Double Salts.** By ALLERTON S. CUSHMAN (*Amer. Chem. J.*, 1901, 26, 505—518. Compare Abstr., 1900, ii, 725).—The author disputes the ground on which Meyer (Abstr., 1900, ii, 655) attributes to thallic chloride the formula  $\text{TlCl}_2\text{Cl}_2$ . The reason why Meyer did not find

that all the chlorine was precipitated by the Volhard method is that the thallic chloride oxidises some thiocyanate with production of potassium cyanide which prevents the complete precipitation of the silver chloride. The views previously expressed are maintained and the constitution of the various complex compounds of thallium chlorides with water are explained by the aid of quadrivalent oxygen.

Thallic chloride cannot be freed from water without undergoing reduction. Thallic chloride is easily soluble in ether, but the crystals separated from the solution have not the formula  $\text{TlCl}_3 \cdot (\text{Et})_2\text{O}$  assumed by Meyer, but  $\text{TlCl}_3 \cdot 4\text{H}_2\text{O}$ . J. McC.

**Theory of the Electrolytic Extraction of Copper.** By JACOB EGLI (*Zeit. anorg. Chem.*, 1902, 30, 18—85).—An historical account is given of the methods which have been proposed for the electrolytic extraction of copper from its ores and the disadvantages which are the causes of the non-success of these are pointed out. In connection with the Marchese process, the electrolytic extraction of copper sulphides by various solvents has been investigated, and in connection with the Höpfner process the electrolysis of cupric chloride solutions has been studied. An artificial cuprous sulphide containing some cupric sulphide was electrolytically extracted with sulphuric acid of sp. gr. 1.225 (acid of maximum conductivity). On electrolysis, the ore being made the anode, a slime is deposited on it which soon stops the current. This slime contains free sulphur, but it is shown from the analysis of the slime progressively deposited that the solution of the copper takes place in the two phases: (a)  $\text{Cu}_2\text{S} + \text{SO}_4'' = \text{CuSO}_4 + \text{CuS}$ , and (b)  $\text{CuS} + \text{SO}_4'' = \text{CuSO}_4 + \text{S}$ . Using current densities up to 30 amperes per sq. dm. the sulphur could not be oxidised. Rise of temperature favours the passage of the current. The same cuprous sulphide was electrolytically extracted with 4.5*N* sodium hydroxide, the sulphide in this case being the cathode. The sulphur passes into solution leaving metallic copper in the residual slime. Since the slime in this case has not a high resistance, the potential remains nearly constant throughout the electrolysis. The current yield is at first good but falls off, and it has further been observed that the current yield decreases as the current density rises. The cathodic slime can then be easily dissolved electrolytically in sulphuric acid, and as it contains little sulphur the previous disturbing factor is removed.

A preliminary experiment showed that cuprous sulphide is scarcely soluble in 5*N* hydrochloric acid, but when chlorine is passed into the acid, rapid solution takes place. The cuprous sulphide was made the anode in an electrolytic extraction with 5*N* hydrochloric acid, and it was found that the copper passes into solution and the sulphur is oxidised to sulphuric acid. The current yield (as measured by means of a copper voltmeter) was found to be considerably more than 100 per cent. (rising to as much as 147 per cent.), and this indicates that even in presence of excess of free chlorine, which was found in the solution, the copper dissolves as cuprous chloride. From the analysis, it is calculated that about 53 per cent. of the dissolved copper existed as cuprous chloride. This has been confirmed by observing the actual formation of insoluble cuprous chloride when a more dilute (0.5*N*)

acid was employed. Cuprous chloride is formed too at all current densities. Addition of sodium chloride favours the electrolysis.

The electrolysis of cupric chloride was carried out with a solution of this substance using a platinum cathode and a carbon anode in a porous cell. When the solution is stirred, it is found that rapid stirring diminishes the yield for a given current, but the copper deposited is purer because the cuprous chloride formed by the dissolving of separated copper by the cupric chloride is washed away from the deposit. In a series of experiments, the solution circulated through the electrolytic cell and passed into another vessel containing a copper plate, and the rate at which the copper dissolved was measured. To obtain constant results, the liquid must always circulate at the same rate. Addition of hydrochloric acid diminishes the current yield, but leads to a pure copper, because the cuprous chloride formed is retained in solution. When the concentration of acid is very great, the current yield begins to increase slightly. Sodium chloride added to the solution also diminishes the current yield, but not to anything like the same extent as hydrochloric acid; the deposited copper is very pure. The current yield diminishes as the concentration of cupric chloride increases, and the copper deposited becomes more impure, for more cuprous chloride is formed, and it may even happen that cuprous chloride alone is deposited. It is not advisable, however, to diminish the concentration too much, for then the copper is deposited in a very spongy form. At a temperature of about  $12^{\circ}$ , the deposited copper is spongy; a coherent deposit is obtained at about  $25^{\circ}$ , but as the temperature rises above this, the current yield diminishes and the deposit is not so pure. Increase of current density slightly increases the current yield, because the solubility of the copper in the electrolyte is almost independent of this density. At very high current densities, however, the current yield falls on account of the separation of hydrogen at the cathode.

A deposit containing up to 99.98 per cent. of copper can be obtained from a solution containing 0.1 gram-mol. of cupric chloride, 0.1 gram-mol. of hydrochloric acid, and 0.4 gram-mol. of sodium chloride per litre.

J. MCC.

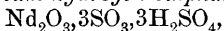
**Nature of Mercuric Iodide in Solution.** By J. H. KASTLE and JEWETT V. REED (*Amer. Chem. J.*, 1902, 27, 209—218. Compare Kastle and Clark, *Abstr.*, 1900, ii, 141).—When a saturated solution of mercuric iodide, prepared by heating the red modification in amyl alcohol at  $150^{\circ}$ , was cooled to  $118^{\circ}$ , red spots began to appear after about ten minutes among the yellow crystals which had previously separated; equilibrium, therefore, is not possible between the yellow variety of mercuric iodide and its saturated solution in amyl alcohol, even at  $10^{\circ}$  below the transition temperature ( $128^{\circ}$ ) of the compound. When, however, saturated solutions of mercuric iodide in naphthalene at  $140^{\circ}$  were cooled to  $100^{\circ}$ , no separation occurred. On addition of crystals of the red modification, the solution was not affected, but if yellow crystals were put into the solution a considerable quantity of yellow crystals immediately separated. The yellow iodide is also precipitated when other substances, such as powdered glass, are added to the

solution, whence it is seen that the separation of the yellow form does not depend only on the action of isomorphous crystals, but is also brought about by the disturbance of an unstable condition of equilibrium in the supersaturated solution of the iodide. These experiments confirm the conclusion previously arrived at, that solutions of mercuric iodide contain the yellow modification. It seems, therefore, that red mercuric iodide is insoluble in organic solvents and that the compound changes into the yellow variety as it passes into solution; this view is supported by the observation that the red modification dissolves more slowly in naphthalene than the yellow variety.

The stability of the yellow mercuric iodide which has separated from a solution varies greatly under different solvents; experiment has shown that the stability increases with the viscosity of the solvent, and that it is greater under vaseline than under any other solvent yet studied. This fact is readily explained, since in viscous solvents all chemical and physical changes are slow, sudden changes of temperature do not occur, and motion and friction of suspended particles are but slight.

E. G.

**Acid and Basic Sulphates of Neodymium and Praseodymium.** By CAMILLE MATIGNON (*Compt. rend.*, 1902, 134, 657—660).—The *neodymium hydrogen sulphate*,  $\text{Nd}(\text{HSO}_4)_3$  or



produced either by evaporating down a solution of the neodymium salt of a volatile acid with excess of sulphuric acid or by dissolving the normal sulphate in the boiling reagent and allowing the solution to cool, crystallises in long, silky, deliquescent, pink needles, which have an oblique extinction inclined at  $12^\circ$  to the principal axis. This form, however, rapidly becomes hydrated and changes into an aggregate of small, anisotropic crystals; finally, the normal salt with  $8\text{H}_2\text{O}$  is obtained mixed with excess of dilute sulphuric acid. One hundred parts of boiling concentrated sulphuric acid dissolve 1.30 parts of the acid salt. The heats of dissolution of the acid and normal sulphates in water at  $16^\circ$  are 64.20 and 37.2 Cal. respectively, the heat of formation of the former from the latter being 26.3 Cal.

The *basic* neodymium sulphate,  $(\text{NdO})_2\text{SO}_4$  or  $\text{Nd}_2\text{O}_3 \cdot \text{SO}_3$ , obtained by gently igniting the normal salt, is an insoluble, amorphous, pink powder stable at  $1000^\circ$ .

The *praseodymium hydrogen sulphate*,  $\text{Pr}(\text{HSO}_4)_3$ , prepared in a similar manner to the corresponding neodymium salt, is isomorphous with this substance, separating in slender needles having oblique extinction; 100 parts of boiling concentrated sulphuric acid dissolve only 1.02 parts of the compound. The heats of dissolution of the acid and normal sulphates in water at  $16^\circ$  are 65.5 and 36.0 Cal. respectively, the heat of formation of the former from the latter being 24.2 Cal. The acid praseodymium salt is less stable than its neodymium analogue, and is more readily decomposed on heating.

The *basic* praseodymium sulphate  $(\text{PrO})_2\text{SO}_4$ , produced by igniting the normal salt at  $1000^\circ$ , is a pale green, insoluble, amorphous powder.

G. T. M.

**Crystalline Forms of Sulphates of Neodymium, Praseodymium, and Samarium.** By HENRI DUFET (*Chem. Centr.*, 1902, i, 452; from *Bull. Soc. franç. Min.*, 24, 373—403. Compare Fock, *Zeit. Kryst. Min.*, 32, 251, and Kraus, *Abstr.*, 1901, ii, 453).—Neodymium sulphate,  $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ , praseodymium sulphate,  $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ , and samarium sulphate,  $\text{Sa}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ , are isomorphous and separate in monoclinic crystals. A crystallographic examination of the sulphates prepared by Chenal and Douilhet gave the following data [ $a:b:c = 0.99465:1:0.88093$ ;  $\beta = 88^\circ 17' 0''$ ], [ $a:b:c = 0.99026:1:0.88278$ ;  $\beta = 88^\circ 24' 10''$ ], and [ $a:b:c = 1.00103:1:0.88192$ ;  $\beta = 88^\circ 16' 40''$ ] respectively. A spectroscopic examination of the salts showed their extreme purity. E. W. W.

**Crystallisation of Peroxide of Iron.** By ALFRED DITTE (*Compt. rend.*, 1902, 134, 507—512).—The author has studied the production of crystalline peroxide of iron when hydrated ferrous sulphate and sodium chloride are fused together, and has shown that the formation of crystals is effected by an interaction between water, hydrogen chloride, and ferrous chloride (as vapour); if the fusion is carried out in an open crucible, little crystalline peroxide of iron is formed. If a little potassium fluoride is added to the mixture, the hydrogen fluoride thus produced greatly aids the production of crystals. The sulphates of nickel, cobalt, and manganese do not yield crystalline oxides when similarly treated, probably because these sulphates become anhydrous at a temperature far below their points of decomposition, whilst ferrous sulphate loses its water of crystallisation only just before it begins to decompose. K. J. P. O.

**Specific Heat and Atomic Weight of Vanadium.** By CAMILLE MATIGNON and E. MONNET (*Compt. rend.*, 1902, 134, 542—545).—Ferrovanadium, obtained by reducing a mixture of iron oxide and vanadic oxide by means of aluminium, is a brilliantly white alloy of fibrous structure, very easily soluble in dilute acids, and capable of imparting a green coloration to water. The specific heat of the alloy between  $15^\circ$  and  $100^\circ$  is 0.1185; from this value, the specific heat of vanadium can be calculated by Regnault's rule, and is 0.1258; the atomic heat is then 6.4, when  $\bar{V} = 51$ .

The specific heat of aluminium-vanadium is 0.1565; the specific heat of vanadium, calculated from this value, is 0.1235, and the atomic heat 6.3.

Vanadium is very accurately estimated by reducing vanadic compounds, by means of sulphurous acid, to hypovanadic oxide,  $\text{V}_2\text{O}_4$ , and titrating the latter with standard potassium permanganate.

K. J. P. O.

**Thermochemistry of the Action of Hydrogen Peroxide on Vanadates and Pervanadates.** By L. PISSARJEWSKY (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 210—216).—The results obtained by the author for the amounts of heat developed by the interaction of potassium vanadate with different proportions of hydrogen peroxide in aqueous solution are as follows:



Mol. of $\text{KVO}_3$ .	Mols. of $\text{H}_2\text{O}_2$ .	Heat developed.
1	1	9.024 Cal.
1	2	17.772 „
1	$3\frac{1}{2}$	17.731 „
1	4	17.521 „

Increase in the amount of hydrogen peroxide beyond 2 mols. to one of the vanadate has thus no influence on the heat developed. Allowing for the heat of formation of hydrogen peroxide from water and oxygen (23,100 Cal.), the heat of formation of potassium pervanadate from the vanadate and oxygen is represented by the equation  $\text{KVO}_3 + \text{O} = \text{KVO}_4 - 14,076 \text{ Cal.}$  Besides the compound  $\text{KVO}_4$ , in which the ratio of V : active oxygen = 1 : 1, there exists in aqueous solution a more highly oxidised compound, in which V : active oxygen = 1 : 2, and this is either a salt of the composition  $\text{KVO}_5$  or a double compound of the composition  $\text{KVO}_4 \cdot \text{H}_2\text{O}_2$ . The last, like the similar compound formed by molybdic acid and having the composition  $\text{MoO}_3 \cdot 2\text{H}_2\text{O}_2$ , is not resolved in solution into hydrogen peroxide and the corresponding acid, but such resolution takes place to a considerable extent with the compound formed by tungstic acid with hydrogen peroxide.

T. H. P.

## Mineralogical Chemistry.

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**Occurrence of Free Sulphur in Beaumont Petroleum.** By CLIFFORD RICHARDSON and EDWIN C. WALLACE (*J. Soc. Chem. Ind.*, 1902, 21, 316—317).—The limestone in which this petroleum occurs contains crystals of sulphur. Its presence explains that of the hydrogen sulphide of the crude oil and the fact that, after removing this by a current of air, it is again formed by heating the oil to 200°.

By passing the oil through a Day's kaolin filter, several fractions are obtained greatly differing in colour, specific gravity, and percentage of sulphur. The most remarkable fact is, however, that the denser fractions, particularly the second, on standing for about one month deposit regular crystals of sulphur. L. DE K.

**Analyses of Bulgarian Minerals.** By FRANTIŠEK KOVÁŘ (*Jahrb. Min.*, 1901, ii, Ref. 362—364; from *Rozpravy České Akad. [Mem. Bohemian Acad.]*, 1900, No. 37, 20 pp.).—I, Spessartite, as reddish grains, sp. gr. 4·19, from a block composed of pyroxene, tremolite and metallic ores (pyrites, magnetite, alabandite) from the Rhodope mountains:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	Total.
37·02	18·83	1·26	6·15	34·57	0·76	1·19	99·78

II, A black, magnetic ore, sp. gr. 4·67, from the gneiss at Debarštica, has, according to analyses II and IIa, the formula  $(\text{Fe,Mg})(\text{Fe,Mn})_2\text{O}_4$ , and is therefore referred to jacobsite :

	Fe.	Mn.	Mg.	Ca.	Insol.	O.	Total.
II.	46·38	19·63	3·46	trace	1·72	[28·81]	100·00
IIa.	45·58	19·29	3·40	trace	3·07	[28·66]	100·00

Chromite from the Rhodope Mountains; analysis III of material as mined in the serpentine, IIIa of material from the river-sands :

	$\text{Cr}_2\text{O}_3$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	FeO.	MnO.	MgO.	CaO.	$\text{SiO}_2$ .	Total.	Sp.gr.
III.	51·05	9·76	—	27·07	trace	8·98	trace	(2·80 serpentine)	99·66	4·49
IIIa.	53·07	10·83	10·27	8·71	—	16·76	0·22	0·35	100·21	4·42

IV, Chrysotile veins in the serpentine of the last-named locality.  
V, Lamellar serpentine :

	$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	FeO.	MnO.	CaO.	MgO.	$\text{H}_2\text{O}$ .	Total.	Sp.gr.
IV.	42·85	0·38	—	2·66	—	0·62	40·23	13·06	99·80	2·51
V.	41·84	0·92	—	2·46	—	trace	40·80	14·19	100·21	2·45
VI.	38·06	22·05	15·18	—	trace	23·06	nil	1·82	100·17	—
VIa.	38·79	26·12	10·33	—	trace	23·30	trace	1·90	100·44	—

VI, prismatic crystals and VIa, columnar aggregates of epidote from crevices in syenite at Philippopel. L. J. S.

**Gibbsite from India.** By H. WARTH (*Min. Mag.*, 1902, 13, 172—173; and *Centr. Min.*, 1902, 176—179).—Beneath the soil which covers the gray, igneous rocks of the Palni Hills in the Madura district of the Madras Presidency, there is a loose bed, about one foot in thickness, of a mineral which is shown by the following analysis (I) to be gibbsite,  $(\text{Al}_2\text{O}_3, 3\text{H}_2\text{O})$ . It is amorphous, and takes the form of nodular plates. In colour it is nearly white with a cream or reddish tint; sp. gr. 2·42. It dissolves easily in hot sulphuric acid and in hot sodium hydroxide solution; less perfectly in hot hydrochloric acid. The mineral has probably been formed by the action of percolating water containing carbon dioxide on alkali aluminate, the latter having been derived from the weathering of the underlying igneous rock :

	$\text{H}_2\text{O}$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	CaO.	MgO.	$\text{TiO}_2$ .	$\text{SiO}_2$ .	Total.
I.	33·74	62·80	0·44	0·20	0·03	0·04	2·78	100·03
II.	16·2	37·3	2·5	0·9	—	—	41·8*	98·7

The second paper gives, in addition, an account of a mineral which occurs abundantly as white nodules in the more or less decomposed igneous rock of the Palni Hills. In composition (anal. II) it is near to kaolin, but it is not plastic like ordinary kaolin, and is more readily attacked by hydrochloric acid than is the latter. L. J. S.

**Occurrence of Chrompicotite in Canada.** By G. CHRISTIAN HOFFMANN (*Amer. J. Sci.*, 1902, [iv], 13, 242—243).—Chrompicotite, hitherto known only from Dun Mountain in New Zealand, has recently

\* Including 2·0 per cent. crystalline silica, and 0·6 per cent. free amorphous silica.

been found in considerable quantity as veins in serpentine on Scottie Creek in the Lillooet district, British Columbia. It is massive, with a coarse, granular structure and a velvet-black colour. In very thin sections it is translucent with a brownish-red colour. Sp. gr. 4.239. Analysis by R. A. A. Johnston gave :

$\text{Cr}_2\text{O}_3$ .	$\text{Al}_2\text{O}_3$ .	FeO.	MgO.	$\text{SiO}_2$ .	Total.
55.90	13.83	14.64	15.01	0.60	99.98

L. J. S.

Analyses [of Dolomite, Ankerite, Forsterite, and Titanomagnetite]. By H. ARSANDAUX (*Bull. Soc. franç. Min.*, 1901, 24, 472—476).—I, Dolomite in Triassic marls at Djelfa, Algeria. II, Dolomite crystals in Triassic gypsum from Haidérenia near Cambo, Basses-Pyrénées. III, Dolomite as drusy crystals lining crevices in dolomite interlaminated with crystallised schists at Vieilleville, Loire-Inférieure. IV, Ankerite crystals with quartz and siderite from Saint Pierre, Alleward : this enclosed veins of calcite which was separated before analysis :

	CaO.	FeO.	MnO.	MgO.	$\text{CO}_2$ .	Total.	Sp. gr.
I.	30.0	2.7	0.6	19.6	46.8	99.7	2.889
II.	30.3	0.9	0.6	20.8	47.8	100.4	2.872
III.	30.0	4.0	0.6	18.7	46.6	99.9	2.910
IV.	28.2	17.2	traces	10.9	42.5	98.8	3.025

All four analyses lead to the formula  $\text{CaCO}_3(\text{Mg}, \text{Fe}, \text{Mn})\text{CO}_3$ .

V, Forsterite from Kandy, Ceylon ; this constitutes the bulk of a compact, greenish-yellow, waxy rock ; small amounts of calcite, phlogopite and serpentinous decomposition products were separated from the material before analysis :

	$\text{SiO}_2$ .	FeO.	MgO.	$\text{TiO}_2$ .	$\text{Fe}_2\text{O}_3$ .	MnO.	Total.	Sp. gr.
V.	42.8	2.6	55.4	—	—	—	100.8	3.248
VI.	—	34.5	0.5	5.3	57.7	0.9	98.9	5.065

VI, titanomagnetite, as magnetic octahedra, from Croustet, near Le Puy, Haute-Loire : formula,  $(\text{FeO}, \text{TiO}_2, \text{Fe}_2\text{O}_3)(\text{Fe}, \text{Mn}, \text{Mg})\text{O}$ .

L. J. S.

[Analyses of Strontianite and Spodumene.] By FRANTIŠEK Kovář (*Jahrb. Min.*, 1901, ii, Ref. 364 ; from *Zeit. Chem. Ind. Prag*, 1900, 6 pp.).—Strontianite as hemispherical, radially fibrous masses occurs with calcite and analcite in cavities in the nepheline-tephrite of Mt. Kunětice, near Pardubitz, Bohemia. Analysis gave :

$\text{CO}_2$ .	SrO.	CaO.	FeO.	$\text{H}_2\text{O}$ .	Insol.
30.67	65.06	3.81	trace	0.09	0.12

Spodumene, as white, very fine needles, occurs in fibrous calcite from Čichov, Moravia ; it was observed as an insoluble residue when the calcite was dissolved. Analysis gave :

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	FeO	CaO.	MgO.	$\text{Li}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	$\text{H}_2\text{O}$ .	Total.
62.70	27.88	0.85	0.29	0.11	5.84	1.78	0.26	99.71

At the same locality, spodumene also occurs as large lamellar masses in crystalline limestone.

The paper also gives the results of analyses of limburgite and limstones. L. J. S.

"Bitter-spars." By K. EISENHUTH (*Zeit. Kryst. Min.*, 1902, 35, 582—607).—Results are given of detailed determinations of the chemical composition, sp. gr., rhombohedral angle and refractive indices of thirty-five specimens of "bitter-spar," mainly from the talc- and chlorite-schists of the Alps. These rhombohedral carbonates, although similar in general appearance, include dolomite, magnesite, breunnerite, calcite, manganiferous dolomite and "brown-spar." In the dolomites, the amount of calcium remains constant, and the formula is  $\text{Ca}(\text{Mg}, \text{Fe}, \text{Mn})(\text{CO}_3)_2$ . The tabulated results show that an increase in the amount of iron in the series is accompanied by an increase in the sp. gr. and the refractive indices, whilst the rhombohedral angle becomes more obtuse. It is shown that magnesite, as well as dolomite, occurs in the Zillertal and in the Pfitschtal, Tyrol. L. J. S.

[Ankerite from Montana.] By WALTER HARVEY WEED (20th *Ann. Rep. U.S. Geol. Survey*, for 1898—1899, 1900, Part III., 409).—The following mineral analyses are given in a monograph (pp. 257—581) on the geology of the Little Belt Mountains, Montana. These are of ankerite, which occurs abundantly as a gangue in the mineral veins of this region. It is coarsely crystalline, and white, or very pale brown or pink; in cavities there are rosette-like aggregates of small, rhombohedral crystals:

$\text{FeCO}_3$ .	$\text{MnCO}_3$ .	$\text{CaCO}_3$ .	$\text{MgCO}_3$ .	Total.	Insol. in HCl (deducted).
26.55	41.26	15.08	17.11	100.00	12.76
15.34	20.62	43.00	21.04	100.00	14.34

The same paper gives the results of many rock analyses. L. J. S.

Apatite from Minot, Maine. By JOHN E. WOLFF and CHARLES PALACHE (*Proc. Amer. Acad. Arts and Sci.*, 1902, 37, 517—528).—A description is given of excellent crystals of transparent, rich purple apatite found associated with quartz, orthoclase, lepidolite, &c., in a cavity in pegmatite at Minot, Maine. As shown by the following analysis, the mineral is fluor-apatite without chlorine: formula,  $\text{Ca}_5(\text{F}, \text{OH})(\text{PO}_4)_3$ . At a temperature of  $320^\circ$ , the crystals become colourless or faintly yellow, the loss of colour being accompanied by decrepitation, phosphorescence and a petroleum-like odour:

$\text{P}_2\text{O}_5$ .	$(\text{Fe}, \text{Al})_2\text{O}_3$ .	$\text{MnO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	$\text{H}_2\text{O}$ .	$\text{F}$ .	Loss at $320^\circ$ .	Total less O for F.
41.30	0.71	0.85	53.43	0.70	0.27	0.36	0.29	2.38	0.04	99.33

The axial ratio ( $c = 0.7348$ ) and the birefringence ( $\omega - \epsilon = 0.0020$ ) are lower than any hitherto recorded for apatite. Sp. gr. = 3.159. A table comparing the numerical values of these physical characters with the percentages of chlorine and fluorine in various apatites indicates that sufficient data have not, as yet, been determined to allow of any

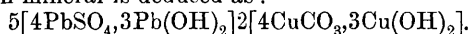
conclusions being drawn as to inter-relations between the physical and chemical characters of apatite. L. J. S.

**Occurrence of Monazite in Iron-ore and in Graphite.** By ORVILLE A. DERBY (*Amer. J. Sci.*, 1902, [iv], 13, 211—212).—Numerous crystallised grains of corundum, monazite and zircon were found enclosed in a specimen of magnetic iron-ore (consisting of a mixture of magnetite and ilmenite) from Brazil. Abundant grains of monazite and zircon were also found in graphite from two Brazilian localities. L. J. S.

**Caledonite from Chili.** By GEORG BERG (*Tschermak Min. Mitth.*, 1901, 20, 390—398).—On specimens of the upper oxidised ores from the silver mines of Challacollo in the desert of Atacama, small crystals of caledonite were noticed associated with chessylite and quartz. In colour, these are of a deep sky-blue, instead of greenish or bluish-green as is usual in caledonite. Analysis gave (after deducting 2·31 per cent. insoluble material consisting mainly of quartz):

PbO.	SO <sub>3</sub> .	CuO.	CO <sub>2</sub> .	H <sub>2</sub> O.
69·18	14·15	9·73	3·16	3·78

The material was quite homogeneous, and the carbon dioxide is not due to admixture of cerussite as previously supposed. Pure splinters of the Scotch caledonite were found to effervesce in acid. The formula for the Chilian mineral is deduced as:



From previously published analyses of the Scotch mineral, the formula,  $4[(\text{Pb}, \text{Cu})(\text{SO}_4, \text{CO}_3)], 3[(\text{Pb}, \text{Cu})(\text{OH})_2]$ , is deduced. L. J. S.

**Schneebergite.** By RUDOLF KOEHLIN (*Tschermak Min. Mitth.*, 1902, 21, 15—22).—Schneebergite was described by Brezina (Abstr., 1882, 150) as a cubic mineral consisting mainly of antimony and calcium together with a little iron. Later it was considered by Eakle and Muthmann (Abstr., 1895, ii, 512) to be only garnet (topazolite). It is now shown that schneebergite (that is, a mineral answering to Brezina's description) and garnet occur together at Schneeberg in the Tyrol. The schneebergite occurs always as octahedra, and the garnet only in grains; the former is infusible before the blowpipe, and the latter fusible. Quantitative analysis of schneebergite showed the presence of antimony, calcium, iron, also bismuth, aluminium, magnesium, potassium, sodium, and traces of arsenic, tin and lead. The following quantitative determinations were made: CaO, 20·14 and 19·91; Fe<sub>2</sub>O<sub>3</sub> + Al<sub>2</sub>O<sub>3</sub>, 8·48; MgO, 0·18 per cent. The refractive index of schneebergite was determined by C. Hlawatsch to be about 2·10.

L. J. S.

**[Lepidolite] from Brassac (Tarn).** By H. ARSANDAUX (*Bull. Soc. franç. Min.*, 1901, 24, 428—432).—The gneiss in the neighbourhood of Brassac is penetrated by veins of granulite and pegmatite in which are garnets and tourmaline. Where the pegmatite has been altered by pneumatolytic action, the lithia-bearing minerals, rubellite (sp. gr. 2·99) and lepidolite, together with apatite have been developed. Sometimes

pseudomorphs after orthoclase consist entirely of a mixture of quartz, rubellite and lepidolite. The lepidolite is present as purplish-violet or pearly-white scales 4 mm. across; analysis gave :

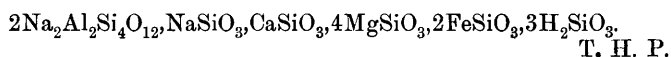
SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	MnO.	(K,Rb,Cs) <sub>2</sub> O.	Li <sub>2</sub> O.	H <sub>2</sub> O.	F.	Total less O for F
51.0	26.2	traces	11.4	5.9	2.2	6.2	100.3

L. J. S.

**Glaucophane from Chateyroux (Gressoney Valley).** By FERRUCCIO ZAMBONINI (*Atti R. Accad. Lincei*, 1902, 11, i, 204—208).—The author describes some shining, black glaucophane crystals showing the forms {110}, {010} and {111}. Analysis gave the following results :

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
55.43	12.26	8.07	2.91	8.67	9.02	2.87	99.23

These numbers correspond with those required for the formula :



**Felspar from Southern Bohemia.** By J. V. ZELIZKO (*Jahrb. Min.*, 1901, ii, Ref. 353; from *Oesterr. Zeit. Berg u. Hüttenw.*, 1900, 48, 7 pp.).—The following analysis of felspar is given in an account of the industry of winning felspar and quartz at various places in the south of Bohemia. The melting point of the felspar is 1420° :

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	MgO.	Fe <sub>2</sub> O <sub>3</sub> .	Total.
67.95	18.60	0.47	9.60	3.16	0.09	trace	99.87

L. J. S.

**Phonolites of Spitzberg, Bohemia.** By HERMANN TRENKLER (*Tschermak Min. Mitth.*, 1901, 20, 129—177).—A petrographical description of the phonolites of the Spitzberg near Brůx, Bohemia, contains the following mineral analyses. I, basaltic hornblende; II, ægirite. Under III is given the composition of the phonolite from which these minerals were isolated.

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	44.05	3.26	14.83	7.12	3.20	—	12.15	12.37	4.08	—	—	101.06
II.	51.75	trace	1.82	23.13	7.01	1.11	5.01	2.09	6.32	1.03	0.71	99.98
III.	56.13	0.81	23.01	1.06		0.18	1.98	1.88	8.67	3.57	2.22	—
	ZrO <sub>2</sub> .	(Ce,La,Di) <sub>2</sub> O <sub>3</sub> .		Cl.	SO <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	CO <sub>2</sub> . Cu. Pb. Sn. Sb. As.					
III.	0.02	0.03		0.12	0.05	0.03	traces					99.56

An account, illustrated with figures of apparatus, is given of the methods employed in separating the minerals of such fine-grained rocks.

L. J. S.

**Density of Fluid and Solid Magmas.** By CORNELIUS DOELTER (*Jahrb. Min.*, 1901, ii, 141—157).—In connection with theories of volcanic action, it is often necessary to know the relative densities of molten and solid rocks and minerals. A summary of the results now obtained is given in the following table. The sp. gr. of the molten

magmas was determined by means of mineral indicators, it being noted which minerals floated and which sank in the magma.

	Natural product.	After ignition.	Fluid.	Rapidly cooled (glassy).	Slowly cooled (crystalline).
Melanite .....	3.75	—	3.55—3.6	3.55—3.60	3.65 —3.7
Augite .....	3.29—3.3	—	2.92	2.92—2.95	3.2 —3.25
Limburgite .....	2.83	2.85—2.88	2.55—2.568	2.55—2.568	2.75 —2.78
Lava, Etna .....	2.83	2.84	2.586—2.74	2.71—2.75	2.81 —2.83
„ Vesuvius ...	2.83—2.85	2.84—2.87	2.68—2.74	2.69—2.75	2.775—2.81
Nephelinite .....	2.735—2.745	2.75	2.70—2.75	2.686	2.72 —2.75
Leucitite .....	2.83	—	2.60—2.68	2.68—2.72	2.75 —2.787

It will be seen from these figures that in all cases the sp. gr. of the molten magma is considerably less than that of the solid crystalline material, but only slightly less than of the solid glassy material.

L. J. S.

**Meteoric Iron from Guatemala.** By STANISLAS MEUNIER (*Compt. rend.*, 1902, 134, 755—756).—A mass of meteoric iron weighing 5.720 kilograms was found in Guatemala in 1901. The structure is lamellar and wanting in compactness; sp. gr. 7.160. Analysis gave:

Fe.	Ni.	Co.	FeS.	Schreibersite.	Total.
89.991	9.052	trace	0.443	0.684	100.170

It belongs to the same type as the Schwetz (Prussia) iron.

L. J. S.



### Physiological Chemistry.

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Effects of Potassium Cyanide and of Lack of Oxygen on the Fertilised Eggs and Embryos of the Sea Urchin (*Arbacia Punctulata*). By E. P. LYON (*Amer. J. Physiol.*, 1902, 7, 56—75).—Development is slightly hastened in very weak solutions of potassium cyanide, but there is a loss of resistance to the poison during development, probably with each cleavage. Prolonged exposure to the poison weakens the union of the cells, and on transference to sea-water the cilia recover, and the cells swim apart. Lack of oxygen produces the same result. Some degree of immunity can be induced by raising the embryos from the start in very weak solutions. W. D. H.

Embryo-chemical Investigations. By P. A. LEVENE (*Zeit. physiol. Chem.*, 1902, 35, 80—83).—The proportion of the different combinations of nitrogen varies with the development of the egg; the following numbers are from experiments on fishes eggs:

	Percentage of total nitrogen.			
	Eggs not incubated.	Incubated for		
		1 day.	10 days.	19 days.
Nitrogen in substances not precipitable by phosphotungstic acid	21.10	21.37	22.72	—
Nitrogen in non-proteid substances precipitable by phosphotungstic acid.....	12.07	25.10	12.48	28.25
Nitrogen in proteids .....	66.00	53.57	64.79	71.84

Hen's eggs incubated for 7 days contain in the yolk monoamino-acids. The analyses given make it probable that there is a mixture of amino-butyric and aminovaleric acids in molecular proportion. W. D. H.

**Hæmoglobin during the Period of Suckling.** By EMIL ABDERHALDEN (*Zeit. physiol. Chem.*, 1902, 34, 500—516).—The absolute quantity of hæmoglobin is smallest at birth, and gradually increases; the increase is rapid when milk is replaced by a diet rich in iron. The relative quantity of hæmoglobin is highest at birth, and gradually falls to the end of the suckling period, when with the new diet it rapidly rises. The amount of iron not present in hæmoglobin is at its maximum about the period of birth, and then falls daily with the increasing absolute amount of hæmoglobin. The tissues, especially the liver and spleen, give a marked iron reaction at birth, the intensity of which lessens daily and practically disappears at the time of weaning. W. D. H.

**Hæmolysis.** By MAX MATTHES (*Chem. Centr.*, 1902, i, 766; from *Münch. Med. Woch.*, 49, 8—10).—Blood corpuscles repeatedly washed in the centrifuge with isotonic salt solution are resistant to pancreatic digestion, and settle with little or no agglutination. If the corpuscles are killed previously with Hayem's sublimate solution, digestion occurs. The same result is noticed with neutralised gastric juice. Rabbit's blood-serum from an animal treated with guinea-pig's blood, which acts hæmolytically on guinea pig's blood, does not lose its hæmolytic properties after pancreatic digestion. The hæmolytic serum itself possesses proteolytic properties. Experiments with heated immune serum show that treatment of the blood corpuscles with immune substance does not kill them or render them digestible by pancreatic juice, but a marked agglutination of the corpuscles is noted. Heating inactive serum for half-an-hour at 56° produces an agglutinating substance, but subsequent treatment with pancreatic juice renders the agglutinating action more apparent. In the serum, substances are present which are able to dissolve the hæmoglobin from the corresponding killed corpuscles; this power is lessened by heat. W. D. H.

**The Inhibition of Hæmolysis by Salts.** By MARKL (*Chem. Centr.*, 1902, i, 730; from *Zeit. Hygiene*, 39, 86—92).—Following up

the work of Hamburger and of Gryns and Hedin, Nolf (Abstr., 1901, ii, 256) has advanced the hypothesis that chemical substances which act hæmolytically do so by producing a hydration of the cells and their membranes, so increasing the permeability of the latter towards hæmoglobin; he finds no evidence of the fermentative nature of the action of alexins on blood corpuscles. Concentrated solutions of such salts, as sodium chloride, potassium iodide, and nitrate, diminish the hæmolytic action of alexins by lowering the permeability of the cell-membranes. Hæmolytic immune serums act by favouring the fixation of alexins in the cells. Pohl, on the other hand (*Arch. internat. Pharmacodyn. Thérap.*, 7, Nos. 1 and 2), has observed that normal serum protects blood corpuscles from poisonous doses of solanine, and considers that this action is not purely physical, as proteid or gum solutions of 2 per cent. strength are as indifferent as physiological saline solution. Solanine increases the hæmolytic action of the serum tenfold; Pohl considers that the protective substance is acid sodium phosphate, for with this salt alone an absolute protection against fifty toxic doses of solanine is obtained. Towards saponin and ichthyotoxin, however, the acid salt is inactive.

The present investigation is concerned with the question whether acid sodium phosphate influences the hæmolysis produced by normal and immune serum. The action of hæmolytic serum only occurs when there is a definite relationship between serum and blood and the anti-hæmolytic action of the acid phosphate is dependent on a definite relationship between this salt and the blood and serum. The concentration of the salt, the temperature and concentration of the blood, are all factors to be considered; high temperature and low concentration of the blood favour hæmolysis; low temperature and high concentration of the blood favour the anti-hæmolytic action of the phosphate. The phosphate, therefore, alters the osmotic relationships of the membranes of the red corpuscles, so that the alexins cannot obtain a footing. This explanation agrees well with Nolf's physical theory.

W. D. H.

**Digestion in the Small Intestine.** By FR. KUTSCHER and J. SEEMANN (*Zeit. physiol. Chem.*, 1902, 34, 528—543).—Normally, tryptic digestion in the intestine breaks up an important part of the proteids into crystalline products, of which leucine, tyrosine, lysine, and arginine were isolated. These products are so changed in their passage through the intestinal wall as to be lost. Proteoses and peptone could not be identified in noteworthy amounts in the intestinal contents.

W. D. H.

**Digestion of Sucrose.** By J. H. WIDDICOMBE (*J. Physiol.*, 1902, 28, 175—180).—The inverting action of intestinal mucous membrane is suspended, but not destroyed, by acid. The portions free from Peyer's patches are more active than those containing the patches. Saliva and extracts of lymph glands have no action on sucrose. The gastric mucous membrane and its juice contain an inverting enzyme, which is active in an acid medium only; the inverting action of the acid of the juice may be got rid of by adding proteid.

W. D. H.

**The Behaviour of Stereo-isomerides in the Animal Body. I. The Fate of the Three Arabinoses in the Rabbit.** By CARL NEUBERG and JULIUS WOHLGEMUTH (*Zeit. physiol. Chem.*, 1902, 35, 41—69).—In rabbits on an ordinary diet, 14·5 per cent. of *l*-arabinose given by the mouth reappeared in the urine; the corresponding number for *d*-arabinose was 39·07; if *r*-arabinose is given, 21·5 per cent. reappears as *r*-arabinose, and 9 per cent. as *d*-arabinose. In rabbits on a diet free from carbohydrates, the numbers are as follows: 14·55 for *l*-arabinose, 31·18 for *d*-arabinose; in the case of *r*-arabinose, 23·5 per cent. reappeared as such, and 5 per cent. as *d*-arabinose. Very similar numbers were obtained if the arabinoses were given subcutaneously; if given intravenously, the numbers are 28·6 for *l*-arabinose, 29·4 for *d*-arabinose; in the case of *r*-arabinose, 18·2 per cent. reappeared as such, and 5·4 as *d*-arabinose; *d*-arabinose leads to no glycogen formation, *r*-arabinose to the formation of small quantities only.

Further experiments were made with arabonates. If sodium *l*-arabonate is given subcutaneously, a certain quantity (not estimated) of *l*-arabonic acid appears in the urine. If sodium *d*-arabonate is given, less of the *d*-acid appears in the urine. In experiments with the alcohols, it was only after *d*- and *r*-arabitol that small quantities of pentose were found in the urine.

A distinction is drawn between rabbits, which are herbivorous, and man. In herbivora, pentosans form part of the normal diet; in man, this is not the case, and his system is fitted to deal more especially with hexoses and their polysaccharides. In herbivora, there appear to be cytases to deal with pentosans. Of the pentoses, *l*-arabinose, the commonest one in herbivorous diet, is most utilised. The close similarity of the formula of *l*-arabinose to that of dextrose is pointed out. One experiment only on man is recorded, which illustrates the change of the racemic pentose into the optically active variety; *r*-arabinose was given by the mouth; 62 per cent. of the excreted arabinose was of the *d*-variety.

W. D. H.

**Does the Pancreas contain an Enzyme which resolves Dextrose into Alcohol and Carbon Dioxide?** By MAXIMILIAN HERZOG (*Beitr. chem. Physiol. Path.*, 1902, 2, 102—124).—This question, which is important in relation to the existence and nature of the glycolytic enzyme, is answered in the negative.

W. D. H.

**Pancreatic Diastase and its Zymogen.** By HORACE M. VERNON (*J. Physiol.*, 1902, 28, 137—155).—Extracts of pancreas made with various media increase in diastatic activity for some days if left in contact with the tissue. This is considered to be due to the gradual conversion of zymogen into enzyme. On keeping, the extracts became acid, especially at a warm temperature, and their diastatic power deteriorated.

W. D. H.

**Absorption of the Nitrogen from Oatmeal in the Dog.** By DIARMID NOËL PATON (*J. Physiol.*, 1902, 28, 119—121).—The amount of proteid not absorbed from oatmeal by the dog is very considerable; it leaves the body by the fæces.

W. D. H.

**Subcutaneous Injections of Dextrose, and Metabolism.** By JAMES SCOTT (*J. Physiol.*, 1902, 28, 107—118).—Injection subcutaneously of 5 to 7 grams of dextrose per kilo. of body weight in dogs causes a marked increase of proteid metabolism. There is a diminution in the proportion of nitrogen which leaves the body as urea. Diphtheria toxin and sulphonal produce similar effects. W. D. H.

**Rôle of Carbohydrates in the Utilisation of Insoluble Salts by the Organism.** By L. VAUDIN (*Ann. Inst. Pasteur*, 1902, 16, 85—93).—When carbohydrates enter into solution, more mineral matter is also dissolved. Thus when bread was subjected to salivary digestion, the amount of ash obtained in the digested portion was double that which was obtained in a control specimen containing no saliva. The increased utilisation of inorganic compounds so brought about chiefly affects salts of the alkaline earths. This is important to both animal and vegetable physiology. W. D. H.

**Phosphate Metabolism.** By OTTO FOLIN and PHILIP A. SHAFFER (*Amer. J. Physiol.*, 1902, 7, 135—151).—The amount of phosphates in the urine was estimated daily in an insane patient, in whom normal days alternated with 'bad days.' During the latter periods, the amount of phosphate is increased. The diet was not kept constant, but an attempt was made to control the result by examining the urine of the attendant, who tried to make his diet coincide with the patient's. The increased excretion is explained on the following hypothesis: on every second day, the system or some part of it (presumably the nervous tissues) is unable to assimilate a part of the phosphate absorbed from the alimentary tract; this non-assimilated phosphate is eliminated the same day. On the alternating days, less is eliminated because the tissues are then repairing the loss sustained on the previous days. W. D. H.

**Nitrogenous Katabolism in the Hedgehog.** By JOSEPH NOÉ (*Compt. rend. Soc. Biol.*, 1902, 54, 227—229).—During the period of hibernation in the hedgehog, the total nitrogen excreted sank to about two-thirds of what it was previously; the amount of urea was lessened by one-half. In spite of the low temperature of the animal, it was not so deeply asleep as to prevent it being fed with its usual amount of meat. The 'xantho-uric' excretion increased somewhat. This is believed to indicate that imperfect oxidation is the main factor concerned in the production of the effects observed. W. D. H.

**The Fate of Uric Acid, administered as such, in the Human Organism.** By FRANZ SOETBEER and JUSSUF IBRAHIM (*Zeit. physiol. Chem.*, 1902, 35, 1—7).—If uric acid in a soluble form is given by the mouth, the greater part is not absorbed, and no modification is produced in nitrogenous metabolism. But if given subcutaneously (dissolved in piperazine solution), it is eliminated quantitatively as uric acid in the urine; this is contrary to what is generally taught, namely, that uric acid given to mammals is excreted as urea. W. D. H.

**Synthetical Formation of Uric Acid in the Animal Organism.** By HUGO WIENER (*Beitr. chem. Physiol. Path.*, 1902, 2, 42—85). —It is generally believed that the formation of uric acid in birds is a synthetical one, from urea or ammonia, and some substance like lactic acid which does not contain nitrogen. There is, however, some evidence to show that in these animals the formation of uric acid is to a small extent oxidative from purine derivatives. In mammals, on the other hand, the formation of the acid is mainly oxidative, but again there is evidence that it may be to a small extent synthetical. If this is so, the difference between the two classes of animals is one of degree rather than of kind. The main object of the present paper is to furnish evidence of the synthetical formation of uric acid in mammals. The first experiments were made with "surviving" organs, finely minced, and mixed with physiological salt solution. If the liver so treated is allowed to remain at 40° for some hours, the amount of uric acid originally present is increased, but if it is previously mixed with spleen or thymus similarly treated, the increase is much more marked. If the spleen or thymus is not mixed with liver, there is a less marked increase in them. This is explicable on the hypothesis that the various organs contain forerunners of uric acid, that the spleen and thymus are rich in these, but are able to form uric acid from them in an oxidative manner only, and that the liver is able in addition to synthesise uric acid from precursors other than purine derivatives. This is supported by the fact that the uric acid in the liver is increased by the addition to it of the residue from alcoholic extracts of the spleen and thymus; such extracts are free from nuclein and purine bases. In order to ascertain what substances soluble in alcohol will lead to this result, ammonium sarcosylate and glycine were added to the minced liver, but did not lead to the formation of more uric acid than in the control specimens. Experiments were therefore performed on hens in order to see what substances will in these birds lead to an increase in uric acid formation. If a certain amount of urea is given by the mouth in the diet to these birds, it is practically all accounted for as uric acid in the urine, but if it is administered subcutaneously the rise in uric acid excretion is not marked; evidently some non-nitrogenous substance must be given also. The following were the substances experimented with, glycerol, propionic acid, hydracrylic acid, lactic acid, pyruvic acid, malonic acid, tartronic acid, mesoxalic acid, butyric acid,  $\alpha$ - and  $\beta$ -hydroxybutyric acids, succinic acid, and malic acid. Each of these substances, by itself without urea, produces no increase in uric acid formation; and mere diuretics like sodium chloride or acetate lead also to a negative result, even if urea is given as well. In each subsequent experiment, 3 grams of urea were given subcutaneously, and the other substance by the mouth; the amount of increased uric acid formed was compared with that theoretically to be expected. In the case of hydracrylic acid, malonic acid, tartronic acid, and mesoxalic acid, the amount formed was the same, or approximately so, as the amount expected; in the case of glycerol, lactic acid (of both kinds), pyruvic acid, glyceric acid, and  $\beta$ -hydroxybutyric acid, the amount of increase varied from 17 to 45 per cent. of that expected; all the other substances mentioned gave a negative result. In other

words, all the substances with a chain of 3 carbon atoms, except propionic acid, were active, and all those with a chain of 4 carbon atoms, except  $\beta$ -hydroxybutyric acid, were inactive in this respect. The relations of the formulæ of the various substances to that of uric acid is pointed out. The ureides of some of these substances, like dialuric acid (tartronylurea) have the same effect. So also have the ordinary articles of diet, such as dextrose, albumin (probably through amino-acids), and fat (probably through its glycerol).

The next question was to apply the knowledge so obtained to mammals. In a dog, if nuclein-free and purine-free food is given, the uric acid excretion sinks to a minimum; it increases somewhat, but not markedly, on the administration of sodium malonate, and also of glycerol. In man, it was found that dialuric acid and sodium malonate have a similar slight effect. Some of the substances in the previous list were not, however, tried; sodium acetate has no such effect. With the isolated minced liver, the following substances were tried: sodium malonate, sodium and ammonium barbiturates, tartronates and dialurates, and glycerol, in conjunction with urea. Positive results were obtained only with tartronic and dialuric acids, and this occurred whether the sodium or ammonium salts were employed; they even produced some increase when urea was not mixed with them. The increase is in no case so great as would theoretically be expected; nevertheless the experiments prove that to some extent the mammalian liver possesses the power of synthesising uric acid from urea and certain non-nitrogenous substances.

W. D. H.

**Correlated Production of Indoxyl and Urea in the Organism.** By JULIUS GNEZDA (*Compt. rend.*, 1902, 134, 485—487).—An examination of the urine of patients suffering from measles, scarlatina, and mental disease showed that the amount of indoxyl excreted is directly proportional to the quantity of urea eliminated, the ratio of these products being approximately 1 mol. of indoxyl to 6 mols. of urea. The indoxyl was estimated in the form of indigo, whilst the urea was determined by the Mörner-Sjöqvist and Kjeldahl processes.

These results indicate that the indoxyl found in the urine is not wholly derived from the putrefactive fermentation occurring in the intestine, but that it is more probably produced by the oxidation of a mol. of proteid substance, this reaction being accompanied by the formation of a definite amount of urea.

G. T. M.

**Condition of the Iron in the Spleen.** By WILLIAM BRODIE BRODIE (*Proc. Roy. Soc. Edin.*, 1902, 24, 21—25).—By micro-chemical methods, iron was shown to exist in the spleen in both intra- and extra-cellular positions. The various proteids obtainable from the spleen were isolated, and each was found to contain iron in the ash.

W. D. H.

**Muscle-plasma in different Classes of the Animal Kingdom.** By HANS PRZIBRAM (*Beitr. chem. Physiol. Path.*, 1902, 2, 143—147).—From the examination of the muscles of thirty animals, 15 invertebrate, 15 vertebrate, the following general conclusions are drawn.

Paramyosinogen (Fürth's myosin) is found in all classes. Myosinogen (Fürth's myogen) is found only in vertebrates; in the cyclostomata, however, this gives no precipitate with sodium salicylate; in other vertebrate classes it does. Soluble myogen fibrin is found immediately after death, and therefore probably during life in fishes and amphibians, but in the remaining classes of vertebrates only in the process of *rigor mortis*. Fürth's myoproteid is found in fishes (selachians, teleosteans) in large quantities, and in the merest traces in amphibians; it is absent in reptiles, birds, and mammals. W. D. H.

**Proteids of Smooth Muscle.** By SWALE VINCENT (*Zeit. physiol. Chem.*, 1902, **34**, 417—429).—The two principal proteids (paramyosinogen and myosinogen) which are found in saline extracts of muscle, are believed to be present in the muscle itself as a proteid coagulable at 47°. Nucleo-proteid is also present; this, however, requires weak alkali to extract it from the muscle. Smooth muscle contains 6 to 8 times the amount of nucleo-proteid contained in voluntary muscle; cardiac muscle contains an intermediate quantity. Unstriated, like striped, muscle gives a salted plasma which coagulates spontaneously, or by dilution; the coagulum consists of the somewhat altered globulin (paramyosinogen) but the other proteid here spoken of as albumin (myosinogen) takes some part in the formation of the clot. The muscle serum contains only such proteids as are derived from the adherent blood, lymph, and connective tissue. W. D. H.

**Effects of Various Solutions on Ciliary and Muscular Movement in the Larvæ of Arenicola and Polygordius.** By RALPH S. LILLIE (*Amer. J. Physiol.*, 1902, **7**, 25—55).—Each of the chlorides of sodium, magnesium, calcium, and potassium exercises a specific influence on contractile tissues, which is evident even in the presence of other salts. Each probably forms a salt-proteid compound (ion-proteid) possessing definite physical properties. For normal activity these must be present in certain definite proportions. These compounds are dissociable, and one salt can be replaced by another. Hence, for instance, the loss of irritability in solutions containing too few sodium ions, and the revival which occurs on subsequent transference to pure solutions of sodium chloride or sea water. Potassium salts are most injurious, because their combinations are not readily dissociable. In solutions of non-electrolytes, the active properties of the tissues are gradually lost; the addition of small quantities of isotonic salt solutions to the non-conductor prevents the immediate loss of the properties which are favoured by the presence of these salts. Development may proceed in favourable artificial mixtures of chlorides of sodium, magnesium, and calcium; it is hindered by the presence of a trace of acid, and furthered by the presence of a trace of alkali.

W. D. H.

**Effects of Solutions of Various Electrolytes and Non-conductors on Rigor Mortis and Heat Rigor.** By ANNE MOORE (*Amer. J. Physiol.*, 1902, **7**, 1—24).—The two proteids in muscle which are capable of coagulation are paramyosinogen and myosinogen,



Hypotonic solutions, and solutions in which much water is absorbed, lower the temperature of coagulation and shorten the time of completion of *rigor*. Acids raise the temperature of opalescence and lower that of coagulation, the amount of lowering increasing with the degree of dissociation. Alkalis have the opposite effect. The effect of various solutions of salts is also described. Calcium does not appear to be essential for the coagulation of the muscle proteids, unless the small amount present in the tissue itself is sufficient, for coagulation takes place in solutions of salts which precipitate calcium, and also in non-conductors. Although the entrance of water favours coagulation, coagulation phenomena cannot be explained entirely on the basis of osmosis. The nature of the ions is a determining factor. Normal *rigor* is not comparable to ordinary contraction, for heat *rigor* may be added algebraically to contraction, and *rigor* is not reversible. Heat *rigor* is not essentially different from normal *rigor*. Normal *rigor* is probably due to the lowering of the temperature of coagulation of muscle proteids caused by acid, water, or certain salts. W. D. H.

**Biltong.** By WILLIAM D. HALLIBURTON (*Brit. Med. J.*, 1902, i, 880—882).—Samples of biltong had the following percentage composition :

Water .....	19.410
Solids .....	80.590
Inorganic solids .....	6.592
Organic solids.....	73.998
Proteids .....	65.866
Fat (ether extract).....	5.140
Glycogen.....	0.133
Sugar .....	0.090
Extractives (by difference) .....	2.769

Biltong is readily digestible in artificial digestive juices, although not quite so readily as fibrin and rabbit's muscle dried at 30°. The tropical sun has possibly some slight coagulating action on the proteid.

W. D. H.

**Cyclic Terpenes and Camphor in the Animal System.** II. By EMIL FROMM and PAUL CLEMENS (*Zeit. physiol. Chem.*, 1902, 34, 385—392. Compare Fromm and Hildebrandt, this vol., ii, 159; Bonani, *ibid.*, ii, 160).—The behaviour of menthol and borneol in the animal system falls under the generalisation previously given. The mentholglycuronic acid was purified in the form of its *barium* salt, which is, however, too hygroscopic for analysis. The *cadmium* salt,  $C_{32}H_{54}O_4Cd \cdot 3H_2O$ , crystallises in small, colourless needles, loses  $1H_2O$  at 100° and becomes anhydrous at 120°. The free *acid* obtained when the cadmium salt is warmed for a short time with dilute sulphuric acid and then extracted with ether, crystallises from water, melts at 87—88°, and contains  $1\frac{1}{2}H_2O$ . When boiled for some time with 10 per cent. sulphuric acid, it is hydrolysed.

Borneolglycuronic acid,  $C_{16}H_{26}O_7$ , melts at 174—175°, and the zinc salt crystallises with  $2H_2O$ . J. J. S.

**Autolysis in Malignant Tumours.** By EUGEN PETRY (*Beitr. chem. Physiol. Path.*, 1902, 2, 94—101).—Carcinomatous tissue (mainly from the breast) if kept at the ordinary temperature (and putrefaction prevented) undergoes autolysis, and among the products, leucine, tyrosine, lysine, and hypoxanthine were identified. Autodigestion is more vigorous than in the normal mammary tissue. The question whether this is a factor to be reckoned with during life was answered in the negative by investigating the newly-removed cancer, and by examining the blood of the patients. Products of proteolysis were not found in the fresh tissue or in the blood.

Injections of extracts of fresh cancer, and of cancerous tissue which had undergone autolysis were made into dogs, and their nitrogenous metabolism examined, but practically no change was found. A hæmolyisin, which has been described as being produced by such tissues during life, was not discovered in the extract used. W. D. H.

**Proteid Decomposition Products in a Degenerated Liver.** By ALONZO ENGLEBERT TAYLOR (*Zeit. physiol. Chem.*, 1902, 34, 580—584).—Acute yellow atrophy of the liver is a disease the cause of which is unknown, and is accompanied by the passage of leucine and tyrosine into the urine. After death, but little of the natural liver substance is discoverable. The liver from a case of this disease was removed 6 hours after death; it weighed 900 grams. It was preserved in alcohol for 3 days, then extracted with ether. The residue from the alcoholic and ethereal extract was freed from fat by treatment with light petroleum, and then extracted with hot water, these extracts were mixed with hot aqueous (neutral and acid) extracts made from the pieces of liver which had been freed from fat by alcohol and ether. It gave no proteid reactions; hexon bases, glutamic acid, and phenylalanine were absent. 0.35 gram of leucine and 0.61 gram of aspartic acid were separated. W. D. H.

**Fat-transference in Phosphorus Poisoning.** By FR. KRAUS and A. SOMMER (*Beitr. chem. Physiol. Path.*, 1902, 2, 86—93).—The relationship of the liver-fat to that of the body has been examined previously in frogs; the present experiments were made on mice. In normal mice, the percentage of fat in the body varied from 14 to 29; the weight of the liver was about 1 gram, and the percentage of fat in it varied from 5 to 12; about 2 per cent. of the total fat in the body was contained in the liver. In mice poisoned by phosphorus, the total weight of the animal was much less, the percentage of fat in the body varied from 4 to 7, the weight of the liver had increased to 1.3—2.2 grams, the percentage of fat in it varied from 7 to 37, and from 20 to 44 per cent. of the total fat of the body was contained in the liver. The observations are considered to show that the chief source of the liver fat is transfer of fat from other parts; it is, however, not absolutely unchanged, for the iodine number of liver fat is higher than that of subcutaneous fat. W. D. H.

**The Poison of the Garden Spider (*Epiria Diadema*).** By HANS SACHS (*Beitr. chem. Physiol. Path.*, 1902, 2, 125—133).—This

poison, named *arachnolysin*, is a hæmolysin, and is identical with what was called toxalbumin by Kobert. Various points in connection with this substance, among which the most important is the production of an antitoxin, have been worked out on the lines of Ehrlich's investigations.

W. D. H.

Physiological Effects of the Poison ("Hypnotoxin") of the Tentacles of Cœlenterata. By P. PORTIER and CHARLES RICHTER (*Compt. rend.*, 1902, 134, 247—248).—Two grams of the fresh filaments sufficed to kill a pigeon weighing 300 grams. The substance does not cause pain, but produces a state of torpor which can only be overcome temporarily and with considerable difficulty. The action of the heart is accelerated. The temperature is lowered by 2—5° and there is generally diarrhœa.

Similar results were obtained with ducks and frogs, and with several groups of *Cœlenterata*.

N. H. J. M.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Effects of the Association of Amylomyces and a Micrococcus.** By PAUL VUILLEMIN (*Compt. rend.*, 1902, 134, 366—368).—In cultivations of *Mucor Rouxianus* and a micrococcus on potatoes, the bacterium developed at the expense of sugar produced by the fungus from starch. A large amount of a yellowish-orange pigment is formed by *Mucor* due to the consumption of maltose by the micrococcus.

N. H. J. M.

**Quantitative Decomposition of Milk Sugar by Bacillus Acidi Lactici.** By PAUL HAACKE (*Arch. Hygiene*, 1902, 42, 16—47).—The products of decomposition of milk sugar by *Bacillus acidi lactici* are lactic acid, acetic acid, and alcohol, together with a gas which was not analysed. The amount of lactic acid obtained never exceeds one-third of the sugar decomposed, and the amount of it present at any moment is not strictly proportional to the sugar decomposed, a portion of the acid being probably further acted on. The amount of sugar decomposed per hour by 1000 bacilli varies according to the conditions from 0.008 to 0.00001 mg.

A. H.

**Study of Lactic Fermentation by Observations of Electrical Resistance.** By PIERRE LESAGE and DONGIER (*Compt. rend.*, 1902, 134, 612—614).—The specific resistance of fresh milk from various cows varies between 230 and 275 ohms and for the same cow varies from 245 to 265 ohms. When the milk is kept, the resistance rapidly diminishes until after about 4 days the milk coagulates, the resistance at this point varying from 185 to 175 ohms whatever the original resistance of the milk. After coagulation, the change in resistance

becomes very slow. The changes are more rapid in open than in closed vessels. The resistance of the whey is about 158 ohms, but this gradually diminishes, especially in open vessels. C. H. B.

**Assimilation of Nitrogen by Plants.** By O. BREFELD (*Chem. Centr.*, 1902, i, 434—435; from *Jahresber. Schles. Ges. vaterl. Kult. Sitz. zool.-bot. Sekt.*, 1901, and *Centr. Bakt. Par.*, 1902, ii, 8, 24—25).—Experiments in sterilised sand with gramineous plants and *Ustilagineæ* *Panicum miliaceum* with *Ustilago destruens*, *Sorghum saccharatum* with *Ustilago sorghi*, and *Setaria italica* with *Ustilago setariae* with mineral manure, with and without nitrogen, showed that no assimilation of free nitrogen took place. N. H. J. M.

**Alinit.** By CARL SCHULZE (*Bied. Centr.*, 1902, 31, 145—147; from *Landw. Jahrb.*, 1900, 30, 319).—The alinit bacillus failed to grow in non-nitrogenous solutions and seems to require organic nitrogenous matter.

Pot experiments were made in which wheat was grown in a mixture of Ellenbach soil with ground sandstone and in sandstone with dextrose. There were three sets of pots (a) sterilised and inoculated with a pure cultivation of the alinit bacteria, (b) sterilised, and (c) not sterilised and not inoculated. It was found at the conclusion of the experiment that moulds were present in nearly all the pots and that the soil contained several foreign bacteria; the alinit bacterium, however, predominated in every case. There was no fixation of free nitrogen, but a distinct loss of nitrogen. A second set of experiments was made to ascertain the effect of carbohydrates. The results were again negative.

Similar results were obtained in pots which were exposed to air.

Field experiments with barley and oats gave negative results.

N. H. J. M.

**Separation of Galactose from Dextrose by *Saccharomyces Ludwigii*.** By PIERRE THOMAS (*Compt. rend.*, 1902, 134, 610—612).—If lactose inverted by means of sulphuric acid is mixed with *Saccharomyces Ludwigii* cultivated in a nutritive liquid containing 5 to 6 per cent. of sucrose and is kept at 25°, all but a minute quantity of the dextrose is decomposed whilst the galactose is practically unaltered. The nitrogenous matter may be precipitated by means of alcohol and the galactose crystallised. It can be purified by repeating the treatment with the yeast. It is important to cultivate the *Saccharomyces Ludwigii* in a liquid containing sucrose, otherwise part of the galactose will be attacked. C. H. B.

**Function of Peroxides in Cell-life. I.** By ROBERT CHODAT and A. BACH (*Ber.*, 1902, 35, 1275—1279).—*Penicillium glaucum*, *Rhizopus nigricans*, and *Sterigmatocystis nigra* are able to flourish in solutions containing 1 per cent. of hydrogen peroxide. The peroxide is not therefore a specific poison, and may play a regular part in cell-life.

T. M. L.

**Respiration of Plants.** By A. FLOROW (*Bied. Centr.*, 1902, 31, 180; from *Bot. Centr.*, 1901, 87, 274).—In experiments with *Mucor*

*mucedo* it was found that the concentration of the organic food affects the amount of dry matter produced. The food values of the different substances employed decrease in the following order: lævulose, dextrose, maltose, saccharose, inulin, ammonium tartrate, and tartaric acid. Removal from the nutritive solution at once greatly reduces the respiration in the case of *Mucor*, as it has no reserve, but has very little immediate effect on *Psalliotia campestris*.

In absence of food, *Amanita muscaria* undergoes a loss of non-nitrogenous matter. There is a production of proteid and nuclein during the period between formation and ripening of spores, followed by a rapid loss of proteids. N. H. J. M.

**Respiration of Plants.** By K. PURJEWICZ (*Bied. Centr.*, 1902, 31, 180—181; from *Bot. Centr.*, 1901, 87, 141).—The respiration quotient increases with the relative amount of oxygen in the food. In the case of carbohydrates, it is generally smaller the greater the mol. weight. With dextrose and sucrose, the quotient increases with the strength of the solutions until a maximum (10 per cent.) is reached, after which it diminishes.

Dextrose, glycerol, mannitol, and lactic acid yield relatively less carbon dioxide in "physiological combustion" than in "chemical combustion." In the case of tartaric acid, the relations are reversed.

In absence of food, the amounts both of carbon dioxide produced and of oxygen absorbed are reduced, but the greater difference is in the case of the carbon dioxide. N. H. J. M.

**Assimilation of some Fungi compared with that of Green Plants.** By THOMAS BOKORNY (*Pflüger's Archiv*, 1902, 89, 454—474).—The assimilation energy, measured by the relative increase in weight per unit of time, is much greater for moulds and yeasts than for green plants. Thus a mould nourished with glycerol and ammonium sulphate increased in weight 1000 times during 28 days. Yeast yields the largest crop in presence of cane sugar when its nitrogenous nourishment is peptone, asparagine being less favourable, and ammonium sulphate least of all. 0.31 gram of dry yeast increased in two days to 0.88 gram in presence of cane sugar and peptone, and to 0.8 gram in presence of peptone without sugar but in a solution which was continually aerated.

The green alga, *Spirogyra*, is capable of obtaining its carbon from sodium formaldehydesulphonate in the absence of carbon dioxide, starch being formed in the cells. Under these conditions, 0.07 gram of the dried alga gave about 0.11 gram in 5 days. A. H.

**Assimilation of Sugar and Alcohol by Eurotyopsis Gayoni.** By PIERRE MAZÉ (*Compt. rend.*, 1902, 134, 191—193. Compare Abstr., 1899, ii, 607).—The results of experiments in which *Eurotyopsis Gayoni* was grown on Raulin solutions containing invert sugar and ethyl alcohol respectively, indicated that in the case of sugar the fungus grows at the expense of the alcohol produced from it. Both the carbon dioxide produced and the oxygen consumed were determined.

The composition of the growth obtained in both cases was similar except as regards percentage of nitrogen, which was rather higher in the fungus grown with alcohol. The composition of the fungus corresponds with that of a substance produced by the union of acetaldehyde (43 mols.) and ammonia (8 mols.). N. H. J. M.

**Assimilation of Lactic Acid and Glycerol by Eurotopsis Gayoni.** By PIERRE MAZÉ (*Compt. rend.*, 1902, 134, 240—242).—*Eurotopsis Gayoni* consumes more lactic acid than glycerol in producing the same weight of substance. In lactic acid solutions, alcohol and carbon dioxide are produced, as well as appreciable amounts of acetaldehyde. The conclusion may be drawn that the plant only utilises the alcohol (after oxidation to acetaldehyde) formed from lactic acid.

In the case of glycerol, more oxygen is consumed than with lactic acid. The hydrogen eliminated from the glycerol is completely oxidised.

The composition of the fungus was the same in both experiments.

N. H. J. M.

**Relations of Calcium and Magnesium to the Growth of Plants.** By W. MAY (*Chem. Centr.*, 1902, i, 365; from *U.S. Dept. Agr. Bul.*, 1901, No. 1, 37—53).—Experiments were made in which various plants were grown in water, sand, and soil, and manured with calcium and magnesium as sulphates, nitrates, and carbonates. A great excess of magnesium was found to be very injurious, and excessive amounts of calcium check the growth. The best relations of calcium to magnesium are 7 : 4.

Calcium should be applied in conjunction with manures which contain much magnesium, or when the soil contains more magnesium than calcium.

N. H. J. M.

**Chemical Modifications in Plants under the Influence of Sodium Chloride.** By EUGENE CHARABOT and ALEXANDRE HÉBERT (*Compt. rend.*, 1902, 134, 181—184. Compare *ibid.*, 132, 159).—The effect of watering peppermint plants with 2·5 per cent. sodium chloride solution was to diminish the percentage loss of water and increase the gain in organic matter more than when no sodium chloride was applied. The essential oil produced in the plants treated with sodium chloride contained more ethers and less menthone than without sodium chloride.

N. H. J. M.

**Supposed New Substances: Pagliari's Olivin and Olivoin.** By P. SPICA (*Gazzetta*, 1902, 34, i, 186—187).—These two substances, obtained by Pagliari (*Movimento farmaceutico*, 1901, Nov., 1—15) from the leaves of the olive, are respectively calcium sulphate and magnesium sulphate.

T. H. P.

**Transformation of Fatty Substances into Sugar in Germinating Oleaginous Seeds.** By PIERRE MAZÉ (*Compt. rend.*, 1902, 134, 309—311).—The results of experiments with earth-nut showed that

a progressive fixation of oxygen took place, with probably a slight loss of carbon, and that sugar is produced from the fat.

N. H. J. M.

**Sugars and Organic Acids contained in some South European Fruits.** By ARTHUR BORNTAEGER (*Zeit. Nahr.-Genussm.*, 1902, 5, 145—155).—The invert (reducing) sugar, the sucrose, and acidity have been estimated in the following fruits:—*Diospyros Lotus*, (Oriental date plum), *Diospyros virginiana* (Virginian date plum), *Diospyros Kaki* (date fig), *Sorbus domestica*, *Mespilus germanica* (medlar), *Arbutus Unedo*, *Musa sapientium* (banana), and *Eryobotrya japonica* (Japanese medlar). All these fruits contained invert sugar varying in the ripe fruits from 4.71 to 16.2 per cent. Sucrose was found only in the unripe fruit of *Arbutus Unedo* (7.34 per cent.), in ripe *Musa sapientium* (7.24 per cent.), and in both the ripe and unripe fruit of *Eryobotrya japonica* (from 2.47 to 4.94 per cent.). The fruits all contained malic acid, but other organic acids, such as oxalic, tartaric, racemic, and citric acid, could not be detected, except in the case of *Eryobotrya japonica*, the juice from the unripe fruit of which contained on the average 1.24 per cent. of citric acid. Tannin was present in *Diospyros Kaki* and *Diospyros Lotus*.

W. P. S.

**Occurrence of Tannin, Starch, and Sugar in First-year Plants of *Acer Pseudoplatanus*.** By J. HÄMMERLE (*Chem. Centr.*, 1902, i, 597; from *Ber. bot. Ges.*, 19, 538—551).—In continuation of previous work by the author and by Berthold, the various parts of the young plants of *Acer Pseudoplatanus* have been tested for the presence of tannin, starch, and sugar from time to time during their early growth and the variations in the amounts of these substances qualitatively determined. The details given in the paper have mainly a botanical interest.

E. W. W.

**Quantity of Indican contained in *Indigofera Tinctoria* and the Manufacture of Indigo.** By AUGUST SCHULTE IM HOFE (*Chem. Centr.*, 1902, i, 672; from *Ber. Deut. Pharm. Ges.*, 1902, 12, 19—30).—Experiments have shown that bacteria do not play any essential part in the production of indigo, the formation of the indigo precipitate not being dependent on the action of these organisms. The original paper contains determinations of the quantity of indican contained in *Indigofera tinctoria* at various periods of growth. The whole of the indican may be extracted from the plant by 2 hours' digestion at 53°, this substance not being decomposed at that temperature. The indican cannot be dissolved from the living plant by water until fermentation has set in, whereby an acid is liberated and the plants are more rapidly killed. As soon as the whole of the oxygen dissolved in the water has been used, the acid fermentation which does not attack the indican gives place to a reducing fermentation by which indican is decomposed and indigo consequently lost. The yield of indigo may be increased by the addition of alkali; the alkali precipitates compounds which dissolve in sulphuric acid, forming red solutions.

E. W. W.



**Conditions of Proteid Formation in Plants.** By W. ZALEWSKI (*Bied. Centr.*, 1902, 31, 166—172; from *Bot. Centr.*, 1901, 87, 277. Compare Abstr., 1901, ii, 619).—In addition to the results obtained with *Allium Cepa* and onions (*loc. cit.*), results obtained with potatoes are described. Tubers when kept in the dark showed little variation in the amount of proteid (percentage of total nitrogen) and the asparagine nitrogen remained very constant.

Decomposition of proteids in seedlings was checked by the presence of ether. In presence of dextrose, decomposition of proteids was greater than production, whilst caffeine increased decomposition.

Leaves of *Helianthus annuus* produced proteids in absence of light from solutions containing nitrates and sugar. N. H. J. M.

**Chemical Composition of *Fragaria Vesca*.** By GIULIO PARIS (*Chem. Zeit.*, 1902, 26, 248—249).—Analyses have been made of the juice of strawberries (*Fragaria vesca*) and the following results obtained:

	I.	II.	III.
Total extract.....	6.56	6.75	7.04
Ash .....	0.65	0.66	0.69
Total acid .....	1.28	1.44	1.36
Citric acid .....	1.17	1.22	—
Malic acid .....	0.14	0.19	—
Reducing sugar.....	3.04	1.28	3.00
Sucrose .....	0.34	1.23	0.51

Analyses I and III were made with scarcely ripe fruit juice, II with juice from quite unripe fruit. No oxalic, tartaric, salicylic, or benzoic acid could be found. J. McC.

**Value of Condiments in the Feeding of Bullocks.** By JOHN A. VOELCKER (*J. Roy. Agr. Soc. Eng.*, 1901, 62, 299—307).—The results of experiments in which bullocks were fed with cake, swedes, oat straw, chaff, and hay, and with the same ration partially replaced by locust bean meal, spice, and cane sugar molasses respectively were, on the whole, not favourable to the use of condiments. Of the three condiments, molasses proved to be the best, but the quantity should not exceed  $\frac{1}{4}$  lb. per head per day. N. H. J. M.

**Alcohol in Milk.** By KURT TEICHERT (*Bied. Centr.*, 1902, 31, 210; from *Landw. Centr. Prov. Posen*, 1901, 234).—Milk from cows fed with slump (90), rye bran (2), linseed cake (1 lb. per day), in addition to oat and rye straw chaff, was found to contain fusel oil. Calves fed with the milk died.

The injury to the milk was shown, by further experiments with cows and sheep, to be due to the slump, which was strongly acid, and yielded 0.9 per cent. of acetic acid when distilled. N. H. J. M.

**Amount of Volatile Fatty Acids in Butter Fat.** By PAUL VIETH (*Bied. Centr.*, 1902, 31, 125—127; from *Milchzeit.*, 1901, 177).—The results of determinations in the milk of four Hanoverian dairies showed that, in the autumn, the Reichert-Meissl number fell to below 25 in

each case, to below 24 in three out of the four, and to below 23 in the case of two dairies (East Friesland).

The highest percentage of volatile fatty acids occurs in the spring, and the amounts decrease to a minimum in October and November. The variations depend partly on the feeding and partly on the period of lactation, the Reichert-Meissl numbers falling as the period of lactation proceeds. N. H. J. M.

**Soaking of Seed Wheat and Seed Barley in Solutions of Sodium Iodide, Bromide, and Chloride.** By JOHN A. VOELCKER (*J. Roy. Agr. Soc. Eng.*, 1901, 62, 326—329).—Solutions containing 1, 10, and 20 per cent. of each salt were employed. The 1 per cent. solutions somewhat benefited wheat; the 20 per cent. solutions and the 10 per cent. iodide solution were injurious. In the case of barley, no beneficial effect was observed after soaking in the 1 per cent. solutions of sodium iodide and bromide and the stronger solutions of the same salts were only slightly injurious. Sodium chloride was, however, distinctly injurious to barley. N. H. J. M.

**Influence of Lithium Chloride on Wheat and Barley.** By JOHN A. VOELCKER (*J. Roy. Agr. Soc. Eng.*, 1901, 62, 318—326. Compare Abstr., 1901, ii, 269).—In the case of wheat, application of lithium chloride (at the rate of 0.5 to 2 cwt. per acre) retarded germination and produced shorter and weaker straw; it also reduced the yield of grain. The effect on barley was to retard growth and to reduce the production of grain; barley straw was not, however, shortened by lithium chloride. N. H. J. M.

**Hard and Soft Wheat.** By JOHN A. VOELCKER (*J. Roy. Agr. Soc. Eng.*, 1901, 62, 332—334).—The production of hard and soft wheat was found to depend on the nature of the soil rather than on the character of the wheat sown (compare Abstr., 1901, ii, 270). N. H. J. M.

**Manurial Experiments with Hops.** By THEODOR REMY (*Bied. Centr.*, 1902, 31, 82—87; *from Blätt, Gersten-, Hopfen-, u-Kartoffelbau*, 1900, 136).—Kainite increased the yield of hops in seven experiments out of nine; in one case, the yield was diminished. The same amount of potassium, in the form of 48 per cent. potassium sulphate, gave in every case an increased yield, and the increase was greater than with kainite. When the amount of potassium sulphate was doubled, the increase was still greater. Potassium sulphate produced hops of better quantity than kainite in nearly every case.

The results of subsequent experiments showed that nitrogenous manure applied to good and inferior soils was favourable as regards yield but less favourable to quality. Phosphoric acid had much less effect. N. H. J. M.

**Edible Fungi.** By ALEXANDER ZEGA (*Chem. Zeit.*, 1902, 26, 10).—Analyses of the following fungi, obtained in the Belgrade market, are given: *Agaricus esculentus* (1 and 2); *Agaricus arvensis* (3 and 4); *Lactarius piperatus* (5—8); *Coprinus comatus* (9):

*Percentage Composition.*

	Weight. (grams)	Water.	Nitrogenous matter.	Fat.	Non-nitrog. extract.	Crude fibre.	Ash.
1.	46	93.41	1.73	0.12	3.54	0.39	0.81
2.	18	94.02	1.69	0.08	3.04	0.41	0.76
3.	102	90.01	6.72	0.18	1.56	0.78	0.75
4.	96	89.12	6.64	0.15	2.62	0.84	0.63
5.	16	84.52	6.86	0.92	3.09	3.62	1.09
6.	12	83.84	7.21	1.12	3.68	3.20	0.95
7.	50	87.26	5.73	1.06	1.88	3.06	1.01
8.	70	86.98	5.96	1.20	1.63	3.34	0.89
9.	78	94.31	2.01	0.09	2.95	0.15	0.49

The fat of *Lactarius piperatus* is a white, crystalline substance, which melts at 67.5° and solidifies at 63°. N. H. J. M.

**Experiments on Potatoes.** By MAX FISCHER (*Bied. Centr.*, 1902, 31, 116—119; from *Fühling's Landw. Zeit.*, 1901, 337 and 361).—Under ordinary conditions, with the most remunerative amounts of manures, potatoes of the largest size should be exclusively used as seed potatoes. When manure is deficient or excessive in quantity, or when the soil is rich, small potatoes may be employed, but on rich soil it is preferable to sow selected large potatoes. N. H. J. M.

**Experiments on Weed Prevention.** By JOHN A. VOELCKER (*J. Roy. Agr. Soc. Eng.*, 1901, 62, 334—341).—The application of copper sulphate to the under side of the leaves destroyed the plants to a very great extent. Treatment with phenol greatly reduced the growth of wild onion without injuring the land; and application of lime in the spring, in conjunction with proper cultivation, was very effective in eradicating the annual chrysanthemum. N. H. J. M.

**Liming Soils from a Physiological Point of View.** By OSCAR LOEW (*Chem. Centr.*, 1902, i, 365; from *U.S. Dept. Agr. Bul.*, 1901, No. 1, 9—35).—Magnesium in soils is only injurious when in considerable excess in relation to calcium, as after application of crude potassium salts. The injurious effect is readily overcome by liming.

Thom's method for the approximate estimation of calcium and magnesium is recommended (extracting the sifted soil with 10 per cent. hydrogen chloride).

When the application of magnesium seems desirable, finely powdered magnesite, or unburnt, powdered limestone containing magnesium are preferable to precipitated basic magnesium carbonate or burnt magnesia. The latter is too readily assimilated and may be injurious. N. H. J. M.

**Manurial Experiments with Precipitated Calcium Phosphate.** By HENRIK G. SÖDERBAUM (*Bied. Centr.*, 1902, 31, 203; from *Med. kongl. Landtb.-Akad. Exper. Stockholm*, No. 67, 1—15).—The phosphate (essentially normal tricalcium phosphate) was pre-

pared electrolytically from apatite and contained  $P_2O_5$ , 35.75, and  $CaO$ , 48.83 per cent., together with calcium carbonate and small amounts of calcium fluoride and chloride. Of the total phosphoric acid, 91 per cent. dissolved in 2 per cent. citric acid.

The results of pot experiments with oats showed that notwithstanding the solubility in citric acid, the phosphate did not contain much available phosphoric acid. The same amount of phosphate applied as basic slag and as superphosphate yielded three to four times as much produce as the precipitated phosphate.

N. H. J. M.

**Pot Experiments on the Manurial Value of Various Phosphates.** By OSCAR KELLNER and O. BÖTTCHER (*Chem. Zeit.*, 1902, 26, 8—9).—The phosphates employed were (1) double superphosphate, (2) Chinchas guano, (3) Lobos guano, (4 and 5) Algerian phosphate A and B, (6) crude Indian bone meal, (7) bone meal freed from fat and (8) the same as (7) but more coarsely ground, (9 and 10) fine and coarse steamed bone meal. The manures 1—5 were employed both with and without addition of calcium carbonate. The soil was a humous sand containing only 0.05 per cent. of phosphoric acid and no chalk. The plants (oats) were manured with nitrogen and potassium.

In presence of calcium carbonate, the effect of the phosphatic manures, especially Algerian phosphates and bone meal, was much diminished.

The relative effect of the water-soluble phosphoric acid of the different phosphates was as follows: (1) 100; (2) 46; (3) 35; (4) 39; (5) 35; (6) 55; (7) 52; (8) 31; (9) 51, and (10) 28.

The relations of superphosphate without and with calcium carbonate were 100:89; and of Algerian phosphate B, 35:10.

N. H. J. M.

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### Analytical Chemistry.

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**The Use of Centrifugal Apparatus for Quantitative Analysis.** By FRITZ STEINITZER (*Zeit. anal. Chem.*, 1902, 41, 100—105).—The precipitates obtained in quantitative analysis can be very rapidly collected and washed by the use of centrifugal apparatus. The vessel employed is a glass tube with a detachable conical bottom of glass, porcelain, or platinum, in which the precipitate collects, and in which it is washed, dried, and weighed. Two to four minutes usually suffice for the collection of the precipitate, and very few washings with small volumes of water are required. M. J. S.

**Litmus-Silk.** By FRIEDRICH EMICH (*Monatsh.*, 1902, 23, 76—80. Compare this vol., ii, 45).—The blue litmus-silk, previously recommended (*loc. cit.*), is hydrolysed by much water and becomes red. A

blue litmus-silk, stable to water but less delicate, can be prepared by soaking the red litmus-silk in lead acetate solution. The blue litmus-silk thus obtained contains much lead oxide, and is a most delicate test for hydrogen sulphide; by its means, 0.0001 mg. of sodium sulphide can be distinctly recognised.

K. J. P. O.

**Preparation of N/100 Potassium Hydroxide and N/2 Alcoholic Potassium Hydroxide.** By OTTO SCHMATOLLA (*Chem. Centr.*, 1902, i, 333; from *Pharm. Zeit.*, 47, 25).—The author prepares N/100 potassium hydroxide by diluting 50.5—51 c.c. of N/10 solution to 500 c.c. and standardising this with a N/10 or N/100 solution of pure oxalic acid, using iodoeosin as indicator. The water should have been well boiled, and must not become turbid on adding a few drops of basic lead acetate. To prepare the N/2 alcoholic solution, 5—6 grams of fused potassium hydroxide are dissolved in 5 c.c. of water, the solution is diluted with absolute alcohol to nearly 100 c.c., and clarified by agitating with 5 grams of dried sodium sulphate. The clear liquid is then poured off, standardised with N/10 hydrochloric or oxalic acid, and suitably diluted. A slight dilution with water before titration is advisable.

L. DE K.

**Reactions for Ozone.** By CARL ARNOLD and CURT MENTZEL (*Ber.*, 1902, 35, 1324—1330).—The various well-known tests for ozone, namely, zinc iodide or potassium iodide and starch, guaiacum tincture, potassium iodide and an indicator for alkalinity, thallium hydroxide, tetramethyl-*p*-phenylenediamine, the phenylenediamines, and silver foil, are adversely criticised, since they are not sufficiently characteristic and all are disturbed by the presence of chlorine, bromine, nitrous acid, or hydrogen peroxide. The best of these tests consists of a paper impregnated with potassium iodide and phenolphthalein or rosolic acid. The authors recommend test papers impregnated with a saturated alcoholic solution of benzidine or tetramethyldi-*p*-aminophenylmethane. The benzidine papers turn brown with ozone, blue with nitrous fumes, blue and then red-brown with chlorine, and do not react with hydrogen peroxide, hydrogen cyanide, ammonia, hydrogen sulphide, or ammonium sulphide. A benzidine paper impregnated with a dilute copper sulphate solution is turned blue by hydrogen cyanide. An alcoholic solution of benzidine containing also a little copper sulphate gives a blue precipitate with very small traces of hydrogen peroxide.

The test papers of tetramethyldi-*p*-aminophenylmethane are even more delicate than the benzidine papers; with ozone they give a violet coloration, with nitrous fumes a straw-yellow, and with chlorine or bromine a deep blue; they do not react with hydrogen peroxide and the delicacy of the ozone reaction is considerably increased by the presence of free acetic acid.

R. H. P.

**Estimation of Sulphates in Urine.** By OTTO FOLIN (*Amer. J. Physiol.*, 1902, 7, 152—154).—Fifty c.c. of urine are mixed in a small Erlenmeyer flask with 0.2 gram of potassium chlorate and 4 c.c. of hydrochloric acid of sp. gr. 1.2, and boiled for 15—20 minutes. Twenty-

five c.c. of a 6 per cent. solution of barium chloride are then added, the mixture kept hot (not boiling) for 45 minutes, and then filtered. The precipitate is washed with hot water, and a few times with hot 5 per cent. solution of ammonium chloride. The moist filter is transferred to a weighed crucible, and 2 or 3 c.c. of alcohol are poured on it and ignited. This dries the filter and prevents sputtering; incineration is now performed and the amount of  $\text{SO}_3$  found by multiplying the weight of barium sulphate by 0.34293.

W. D. H.

**Gravimetric Estimation of Gaseous Nitrogen.** By ALEXANDER P. LIDOFF (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 42—51).—The author's method, described in detail in this paper, consists essentially in passing the nitrogenous gas over a mixture of 1 part of powdered magnesium and 3.5—4 parts of freshly ignited lime heated to redness in a bulb tube of hard glass. The magnesium nitride thus obtained is decomposed by water in presence of potassium hydroxide, the ammonia formed being then distilled over into standard sulphuric acid, the excess of which is afterwards determined by titration. A number of measurements show that the method gives results much more accurate than those obtained by the ordinary method of determining nitrogen.

T. H. P.

**Behaviour of Nitric and Nitrous Acids towards a Solution of Brucine in Sulphuric Acid.** By LUDWIG W. WINKLER (*Zeit. angew. Chem.*, 1902, **15**, 170—172).—A reply to Lunge (this vol., ii, 288). The author communicates a series of experiments showing that nitrites react quite as energetically as nitrates with brucine if only a moderate amount of free sulphuric acid is used.

L. DE K.

**Estimation of Citrate-insoluble Phosphoric Acid.** By C. D. HARRIS (*J. Amer. Chem. Soc.*, 1902, **24**, 25—27).—A criticism of the method until recently in use in the laboratory of the North Carolina Department of Agriculture.

The author uses the following arrangement for collecting the residue insoluble in solution of ammonium citrate of sp. gr. 1.09 at 65°. A carbon filter is taken and in the bottom of it is placed a tightly-fitting perforated porcelain disc to which is attached a small wire extending down beyond the small end of the carbon filter. A rubber stopper is then fitted tightly in a pressure bottle and the carbon filter passed through it. A layer of asbestos is placed on the disc in the carbon filter and pressure is applied.

The insoluble matter after being washed is dissolved in a mixture of two volumes of nitric acid and one volume of hydrochloric acid, and then boiled down to a small volume. After diluting to a definite bulk, an aliquot part of the solution containing about 0.4 gram of the original sample is nearly neutralised with ammonia, 10 or 12 grams of ammonium nitrate are added, and the phosphoric acid precipitated with the usual molybdic solution, the precipitation being accelerated by means of Wagner's shaking apparatus. Antimony rubber stoppers are recommended. Finally, the yellow precipitate is titrated.

L. DE K.

**Detection of Arsenic.** By CARL ARNOLD and CURT MENTZEL (*Chem. Centr.*, 1902, i, 600—601; from *Pharm. Zeit.*, 47, 101).—The process recommended by Seybel and Wikander (this vol., ii, 289) when applied to hydrochloric acid does not answer unless this has a strength of more than 22 per cent.; if less, it will be necessary to add some sulphuric acid.

To detect traces of arsenic in compounds of barium, calcium, strontium, mercury, and antimony compounds, these should be boiled with a solution of sodium carbonate and the filtrate evaporated to a small bulk. This should be free from all compounds which decompose or precipitate potassium iodide.

A few c.c. of the acid to be tested or of the alkaline solution are mixed in a wide test-tube with a few drops of a 50 per cent. solution of potassium iodide, the tube is cooled, and one-third of the volume of sulphuric acid slowly added. A yellow precipitate points to arsenic (formation of arsenic tri-iodide), a yellow or reddish coloration is merely due to free iodine.

L. DE K.

**Selmi's Process for the Toxicological Detection of Arsenic.** By GUIDO GIUDICE (*Gazzetta*, 1902, 34, i, 164—172. Compare Abstr., 1881, 311).—It was found by Oglialoro and Forte (*Rendic. Reale Accad. Sci. fis.-math. Napoli*, Dec. 1896) that if antimony is present in any matter submitted to Selmi's test, this metal passes over as volatile chloride with the arsenic, even when the temperature of the bath is kept at 130°. The author has carried out tests with a liquid containing arsenious acid in the presence of salts of tin, mercury, or antimony. Neither mercury nor tin passes over with the arsenic, whilst for antimony Oglialoro and Forte's result is confirmed, with the addition that the antimony is prevented from passing over by keeping the bath at a temperature of 115°. Weighing the arsenic mirror obtained by Marsh's method is not a satisfactory way of estimating the element.

T. H. P.

**Simple Method for the Estimation of Boric Acid.** By A. HEEBERAND (*Zeit. Nahr.-Genussm.*, 1902, 5, 55—58).—The aqueous solution containing the boric acid is made feebly alkaline with sodium hydroxide and evaporated to dryness in a platinum basin. The residue obtained is ignited until all carbonaceous matter has disappeared; it is then dissolved in 5 c.c. of water containing 0.5 c.c. of hydrochloric acid and transferred to a test-tube. The basin is rinsed out with 15 c.c. of alcohol, which are also added to the contents of the test-tube, 15 c.c. of hydrochloric acid of sp. gr. 1.12 are then added, and, after cooling, 0.2 c.c. of a 1 per cent. solution of turmeric. On standing for half-an-hour, should boric acid be present, a coloration is produced, varying in tint from light brown to bright red. The colour thus obtained may be compared with that produced in tubes containing known amounts of boric acid. The presence of 0.1 mg. of the latter gives a feeble brown tint, whilst 10 mg. yield a bright rose red colour. The coloration is somewhat fugitive, and is destroyed by prolonged exposure to light, and also by boiling.

W. P. S.



**Spectroscopic Estimation of Boric Acid, especially in Mineral Waters.** By F. MURARO (*Gazzetta*, 1902, 32, i, 173—178).—The author has investigated the conditions under which Föhr's spectroscopic method (*Zeit. anal. Chem.*, 1887, 26, 79) can be applied to the determination of boric acid in mineral waters. It is found that, before applying this method, the non-alkaline metals must be removed from the solution as also must calcium. The former may be got rid of by the method proposed by Parmentier (*Abstr.*, 1891, 1551), whilst calcium salts may then be precipitated by means of ammoniacal ammonium carbonate, the filtrate being afterwards evaporated to dryness, ignited, and re-dissolved in water. If much magnesium is present, the solution must further be treated with just the amount of potassium carbonate required to precipitate this metal. Where calcium salts are present only in small proportion, whilst the water contains relatively much boric acid, both the magnesium and calcium may be precipitated directly by potassium carbonate.

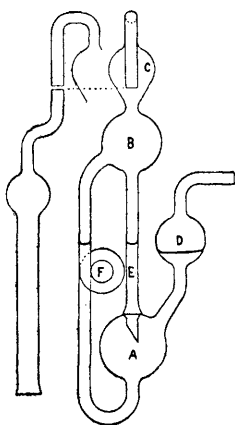
T. H. P.

**Estimation of Carbon in Steel by Direct Combustion.** By RUDOLF L. LEFFLER (*Chem. News*, 1902, 85, 121—122).—The steel borings are sifted, and 2.5 grams of the portion passing a 20-mesh sieve, but retained by a 40-mesh, are mixed with 6 grams of red lead, placed in a porcelain boat, and after drying in a water-bath, are burnt in a porcelain tube, partially filled with copper oxide. The tube is provided with arrangements for purifying the inlet air, and with the usual calcium chloride tube and potash bulbs. A hot furnace is necessary for the combustion. Special steels, such as tungsten steel, do not require sifting.

D. A. L.

**New Design for Potash Bulbs.** By J. N. TERVET (*Chem. News*, 1902, 85, 112—113).—The apparatus consists of two main bulbs, *A*, *B*, and two guard bulbs, *C*, *D*, connected as shown in the figure; the level of the potash when not in use is also indicated. When in use, the gas enters at *D* and forces the potash up *E* into *B*, until the oblique cut at the bottom of *E* is exposed, when the gas bubbles up through *E*, whilst the potash drains from *B* down the syphon tube *F* back into *A*. In this manner, a circulation favourable to the uniform utilisation of the potash and to the thorough washing of the gas is maintained.

D. A. L.



**Estimation of Silicon in High-Grade Ferro-Silicons, by Means of Sodium Dioxide.** By CHARLES RAMORINO (*Chem. Centr.*, 1902, i, 333; from *Mon. Sci.*, [iv], 16, i, 18).—To prevent the violent reaction which takes place when sodium dioxide acts on ferro-silicon, the author operates as follows: 0.5 gram of the powdered sample is mixed with 10 grams of potassium sodium carbonate and 1 gram of

sodium dioxide and slowly heated; the decomposition is complete in a short time. The mass is boiled with water, and a little hydrochloric acid, mixed with 10 c.c. of nitric acid and 2 grams of potassium chlorate, evaporated to dryness and the residue dried at  $110^{\circ}$ . After boiling with 20 c.c. of hydrochloric acid and 200 c.c. of water, the silica is collected, washed, dried, ignited, and weighed. The filtrate may be used for the estimation of sulphur and manganese.

L. DE K.

**Estimation of Alkali Hydroxide or Hydrogen Carbonate in the Presence of Normal Alkali Carbonate.** By BARKER NORTH and W. C. LEE (*J. Soc. Chem. Ind.*, 1902, 21, 322—325).—Thompson's method of estimating alkali hydroxide in the presence of normal carbonate by first titrating with normal acid in the presence of phenolphthalein and then finishing the titration with methyl-orange as indicator, has been criticised by Ridenour (this vol., ii, 49), who uses a certain factor to compensate for what he believes to be a constant error. The authors state that good results may be obtained by working in daylight and immersing the point of the burette in the liquid so as to prevent escape of carbon dioxide in the first stage of the titration. They also found that Robertson's statement as to the influence of large quantities of sodium chloride is correct, but the amount needful to cause error is far above that which is likely to occur in samples of soda ash.

The process as applied to soda ash is briefly as follows: 5 to 10 grams of the sample are dissolved and made up to 250 c.c. Fifty c.c. are then titrated with *N* acid, using phenolphthalein as indicator, and the neutralisation then completed by the aid of methyl-orange. If the amount of acid used in the first stage of the titration exceeds that of the second, the sample contains sodium hydroxide, but if it should be less, this shows the presence of sodium hydrogen carbonate; the difference in acid is then calculated into either of these.

Moisture is estimated by ignition, allowance being made for carbon dioxide expelled from any alkali hydrogen carbonate. L. DE K.

**Determination of Calcium as Oxalate.** By W. PAGIREFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 195—199).—In place of the ordinary procedure in the precipitation of calcium as oxalate, the author suggests a new method, consisting in adding an excess of oxalic acid to a neutral solution of the calcium salt and then neutralising with ammonia. The precipitate thus formed is more coarse-grained than that obtained in the ordinary way, can be readily separated and washed and does not pass through the filter; the composition of the precipitate obtained by either method is  $\text{CaC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ . Should much magnesium be present, the calcium oxalate should be dissolved in acid and reprecipitated as usual. T. H. P.

**Detection of Magnesia in Calcium Oxalate Precipitates.** By H. TÄUBNER (*Chem. Zeit.*, 1902, 26, 246).—As magnesium oxalate is somewhat more soluble in water than calcium oxalate, the washings of calcium oxalate contaminated with magnesia will continue to become turbid on adding silver nitrate. This turbidity is due to silver oxalate and disappears on adding nitric acid.

Should this be the case, it may be taken for granted that the calcium oxalate is contaminated with magnesium oxalate, and it should be purified by dissolving in hydrochloric acid and reprecipitating with ammonia. L. DE K.

**Influence of the Amount of Iron when Zinc is Titrated with Sodium Sulphide.** By A. COPPALLE (*Ann. Chim. anal.*, 1902, 7, 94—96).—In the modified Schaffner process for the volumetric estimation of zinc with standard sodium sulphide, no notice is taken of the volume occupied by the ferric hydroxide, it being generally believed that the error thus introduced is fairly compensated by the retention of some zinc in the precipitate. The author having made a long series of experiments, confirms the statement of Prost and Hassreidter that in order to get really trustworthy results the sodium sulphide should be checked with a standard zinc solution containing the same amount of iron as the zinc ore actually taken for analysis. L. DE K.

**Volumetric Estimation of Thallium.** By VICTOR THOMAS (*Compt. rend.*, 1902, 134, 655—657. Compare *Abstr.*, 1900, ii, 442).—A solution of thallic chloride is treated successively with excess of standard sodium thiosulphate solution, potassium iodide, and starch emulsion, the product being titrated with standard iodine solution. When the thallic solution is concentrated, the operation is conducted in a closed vessel, the precipitated thallous iodide being coagulated by agitation before the final titration. The results are accurate and are not affected by the presence of ammonium and alkali salts or excess of potassium iodide; the method is applicable to solutions of widely different concentration. G. T. M.

**Electrolytic Estimation of Copper in Iron.** By H. KOCH (*Zeit. anal. Chem.*, 1902, 41, 105—107).—Not less than 100 grams of the iron are dissolved in dilute sulphuric acid (400 c.c. of 30° Be) and the insoluble residue collected on a filter. If the substance is an iron rich in carbon, it is well to wash back the residue into the beaker and boil it with 200 c.c. of fresh sulphuric acid to ensure the solution of the last traces of iron, then return it to the same filter, wash, dry, and ignite. It is then dissolved in hydrochloric acid, the solution evaporated to dryness with sulphuric acid, redissolved in 20 c.c. of water and 20 c.c. of nitric acid of sp. gr. 1.2, and after diluting to 120 c.c. and adding a few drops of oxalic acid, it is electrolysed for 9—10 hours with a current density of 0.094 ampere per square centimetre. M. J. S.

**Influence of Hydrochloric Acid on the Precipitation of Cuprous Thiocyanate.** By R. G. VAN NAME (*Amer. J. Sci.*, 1902, 13, 20—26).—The author has previously stated (*Abstr.*, 1901, ii, 130) that free sulphuric or hydrochloric acid does not interfere with the precipitation of copper by ammonium thiocyanate. This point has been further investigated as regards hydrochloric acid, with the following results.

If only a small excess of ammonium thiocyanate is used, the free

hydrochloric acid remaining should not exceed 0.5 per cent. by volume, but a much larger amount may be present if the thiocyanate is used in decided excess; this is also advisable if ammonium salts are present. It is, on the whole, better to neutralise the greater part of the hydrochloric acid by addition of ammonium hydrogen sulphite or ammonia, or both, before precipitating the copper. L. DE K.

**Estimation of Copper as Cuprous Thiocyanate in the Presence of Bismuth, Antimony, Tin, and Arsenic.** By R. G. VAN NAME (*Amer. J. Sci.*, 1902, 13, 138—144).—Copper may be separated from arsenic, bismuth, tin, and antimony by the thiocyanate process, but in the presence of the last three metals the amount of hydrochloric acid required to prevent their precipitation interferes with the exact estimation of the copper (see preceding abstract). The amount of hydrochloric acid required may, however, be reduced to a minimum by adding 1 to 2 grams of tartaric acid.

In the presence of bismuth, an excess of ammonium hydrogen sulphite should be avoided, to prevent precipitation of that metal. After adding the tartaric acid and diluting to a definite volume, small aliquot parts of the solution are tried with the sulphite to find out how much of this may be safely added without causing the bismuth to precipitate. The main solution is then mixed with solution of ammonium hydrogen sulphite and excess of ammonium thiocyanate to precipitate the copper. In the author's experiments, the joint amount of metals was about 0.8 gram and the volume of the liquid after adding the reagents 500 c.c. L. DE K.

**Analysis of Pyritic Residues.** By A. MINOZZI (*Chem. News*, 1902, 85, 123—124).—The *sulphur* in the residues is estimated by a modification of Deutecom's method (*Abstr.*, 1880, 744). Two grams of the pyritic residue are intimately mixed in a platinum crucible with 5 grams of a mixture containing 2 parts of sodium carbonate and 1 part of potassium chlorate, 2 grams of the same mixture being spread over the whole. Heat is quickly applied, until the top layer of mixture fuses, then gradually increased and kept at the maximum, while the mass, from a pasty condition, becomes solid, then semi-fluid, and finally pasty again. When cool, the crucible with its contents is digested with 300 c.c. of warm water until the mass is completely disintegrated. The liquid is decanted through a filter, and the residue washed five or six times by decantation, each time with 50 c.c. of a 2 per cent. solution of sodium carbonate, and finally boiled; the last wash water should contain no sulphuric acid. The sulphuric acid is estimated in the combined solutions as barium sulphate. To estimate the *silica*, *lead*, *titanium*, *copper*, and *iron*, 5 grams of the pyritic residues are gently heated in a platinum crucible, while 25 grams of potassium hydrogen sulphate are gradually added; the mass is then fused. The cooled mass is treated with 500 c.c. of 2 per cent. sulphuric acid and filtered, the residue is washed with boiling water containing a small quantity of sulphuric acid, dried, ignited, and weighed. It is then moistened with 5 c.c. of 10 per cent. sulphuric acid, carefully evaporated with 20 per cent. hydrofluoric acid, treated with a small quantity of am-

monium carbonate, and ignited to constant weight; the loss is silica. The residue is fused with potassium hydrogen sulphate, digested with sulphuric acid, the solution added to the main solution whilst the residue is treated several times with a boiling concentrated solution of ammonium acetate or tartrate. The *lead* is precipitated from this solution by hydrogen sulphide, redissolved in nitric acid, and estimated as sulphate. In 100 c.c. of the main solution, the *iron* is estimated by permanganate either directly or after separation as basic carbonate when manganese, zinc, and other metals are present. The remainder of the main solution is concentrated to 300 c.c., put into a 600 c.c. flask, neutralised with ammonia, slightly acidified with hydrochloric acid and treated with sodium hydrogen sulphite. The precipitate is washed with boiling water, fused with 2 grams of a mixture of 2 parts of sodium carbonate and 1 part of potassium nitrate, the mass digested with 200 c.c. of boiling water, and any *phosphate* estimated in the solution in the usual manner; the residue is fused with potassium hydrogen sulphate, the treatment with sodium hydrogen sulphite repeated, and the *titanic acid* ignited and weighed. The solution free from phosphoric and titanic acids is treated with a small quantity of sodium hydrogen sulphite acidified with 50 c.c. of 10 per cent. hydrochloric acid, and while warm hydrogen sulphide is passed through, and the *copper* in the precipitate estimated. D. A. L.

**Assay of Dalmatian Mercury Ores.** By C. EHRMANN and J. SLAUS-KANTSCHIDER (*Chem. Zeit.*, 1902, 26, 201—202).—These ores contain only a small percentage of mercury; the bulk consists of heavy spar. Eschka's process (condensation of the sublimed mercury on a golden lid) did not always give satisfactory results, so the following process was devised.

One gram of the finely powdered ore is heated with a little strong nitric acid and then dissolved by adding hydrochloric acid and warming until the odour of chlorine has disappeared. After diluting to 250 c.c., 100 c.c. (0.4 gram of sample) of the filtrate are precipitated with hydrogen sulphide, and the sulphides collected in a Gooch crucible containing asbestos and washed with hot water. The precipitate is dissolved in hydrochloric acid containing bromine, the excess of the latter removed by a current of carbon dioxide, and the metals are again precipitated with hydrogen sulphide. After washing with hot water, any metals of the arsenic group are removed by digesting the precipitate with yellow ammonium sulphide. Finally, the sulphides are heated with dilute nitric acid (1 : 3) which dissolves any copper or lead sulphide and leaves mercuric sulphide undissolved. This is freed from any free sulphur by digestion with solution of sodium sulphite and from any traces of lead sulphate by heating with ammonium acetate. After being well washed with hot water, it is dried at 100° and weighed. The crucible may be ignited and reweighed. L. DE K.

**Detection of Mercury in Urine.** By AUGUST LAQUEUR (*Chem. Centr.*, 1902, i, 500—501; from *Charité-Ann.*, 26).—Cazeneuve's test with diphenylcarbazine (Abstr., 1900, ii, 627), although very delicate in aqueous solutions, is not delicate enough for the detection of traces

of mercury in urine. The reaction is greatly improved by first rendering the urine strongly alkaline with sodium hydroxide, but even then it should contain a minimum of 0.19 gram of mercuric chloride per litre, a quantity not likely to occur unless in cases of serious poisoning by corrosive sublimate. L. DE K.

**Action of Bismuth Oxide on various Metallic Solutions.** By JULES ALOY (*Bull. Soc. Chim.*, 1902, [iii], 27, 136—137).—In opposition to the statement made by Lebaigue (*J. Pharm. Chim.*, 1861, 39, 51) that oxide of bismuth when boiled for about a quarter of an hour with metallic solutions precipitates iron (ferric), chromium, and aluminium in the form of their oxides but is without action on ferrous iron, cobalt, nickel, copper, zinc, and lead, the author shows that the precipitation of the former metals is complete only under certain conditions, and that the other metals are partially precipitated either as oxides or as basic salts. Lebaigue's proposal therefore, to employ the method for the separation of the metals in analysis, cannot be adopted. A. F.

**Action of Sodium Peroxide on the Metals of Platinum Ore.** By EMILE LEIDIÉ and QUENNESSEN (*Bull. Soc. Chim.*, 1902, [iii], 27, 179—183. Compare Abstr., 1901, ii, 62, 695).—When the metals of the platinum group are heated to a low red heat (best in a nickel dish) with sodium peroxide, sodium osmate, sodium per-ruthenate, sodium palladate, and basic sodium iridate are formed, all of which are soluble in water, the first three with a yellow, the last with a blue, coloration; platinum and rhodium yield compounds insoluble in water. On the basis of the above behaviour, and of the properties of the substances produced, the authors have drawn up a table for the detection and the characterisation of the different metals in the platinum ore. A. F.

**Study of Fatty Acids in Contaminated Waters.** By HENRI CAUSSE (*Compt. rend.*, 1902, 134, 481—483).—The fatty acids present in contaminated waters are derived from sewage matter, the effluents of certain industries, and the decomposition of proteids. The acids are removed from the water in the form of their insoluble barium salts. These are collected and decomposed by dilute sulphuric or phosphoric acid and the product distilled under diminished pressure. The distillate is milky when the original water is contaminated; it becomes turbid and may even yield a precipitate when treated with basic lead acetate, ammoniacal barium chloride, or neutral mercurio-mercuric nitrate. The fatty acids may also be detected by extracting the distillate with chloroform and examining the residue left after evaporating the solvent; a mass of acicular crystals can be distinguished under the microscope. The acids may be isolated from the barium salts by boiling these with excess of sodium carbonate solution, filtering off the barium carbonate, acidifying the filtrate and extracting with chloroform. The fatty acids present in contaminated waters restore the colour to violet decolorised by sulphurous acid and develop a pale yellow coloration with sodium diazobenzenesulphonate. G. T. M.

**Estimation of Prussian Blue in Spent Gas-purifying Material.** By OSCAR BERNHEIMER and F. SCHIFF (*Chem. Zeit.*, 1902, 26, 227—228).—The alkaline solution containing the ferrocyanide radicle is precipitated with a strongly acid solution of ferric chloride; the excess of acid and iron is removed by washing with boiling water containing 0.5 per cent. of ammonium nitrate, and the prussian blue precipitate is ignited. It leaves practically pure ferric oxide, which corresponds with its own weight of crystallised potassium ferrocyanide, from which the amount of ferric ferrocyanide may then be calculated.

The results obtained are a trifle higher than those obtained by Knoblauch's titration process with copper sulphate, but the authors think they are nearer the truth. The experiments will be continued.

L. DE K.

**Modified Permanganate Method for the Assay of Commercial Glycerol.** By J. GAILHAT (*Chem. Centr.*, 1902, i, 544; from *Mon. sci.*, [iv], 16, i, 89—106).—Purified glycerol is diluted with about 20 per cent. of water, and its sp. gr. is then taken. By means of this liquid, a dilute glycerol is prepared containing 5.9 grams of anhydrous glycerol per litre. The sample to be tested, freed, if necessary, from objectionable products by means of silver nitrate and lead acetate, is also diluted to about the above strength. Both liquids are now titrated by boiling 25 c.c. of each with a mixture of potassium permanganate, manganous sulphate, and dilute sulphuric acid for half-an-hour in a reflux apparatus; 10 c.c. of  $N/2$  oxalic acid are added, and the excess of this is titrated with  $N/10$  potassium permanganate. The exact amount of available oxygen in the permanganate mixture is also estimated by means of oxalic acid and  $N/10$  permanganate. The amount of glycerol in the sample is then found by a simple calculation.

L. DE K.

**Nitroglycerol in an Exhumed Body.** By G. G. POND (*J. Amer. Chem. Soc.*, 1902, 24, 18—20).—The poison was isolated by heating the comminuted material (one-fourth of the stomach and contents) in a current of steam after adding 50 c.c. of water and acidifying with tartaric acid (Dragendorff's process). The turbid distillate was extracted with ether, and the oily residue left on evaporating the ethereal solution gave the usual tests for nitroglycerol, the most characteristic one being the explosions occurring when heated on a platinum spoon, or when struck on an anvil. The weight amounted to 0.0095 gram.

L. DE K.

**Polarimetric Determination of Lactose.** By A. PEYTOUREAU (*Ann. Chim. anal.*, 1902, 7, 88—91).—A criticism of the method described by Denigès for estimating crystallised lactose in milk by polarisation after removing the proteids by the aid of picric and acetic acids, (*Précis de Chimie analytique*, 1898, 686).

The author uses a 20 cm. tube and substitutes the equation  $x = 2DD'/D - D' \times 0.062$  gram for  $x = 2DD'/2D - D' \times 0.062$  gram.

L. DE K.

**Estimation of Raffinose.** By GUSTAV REINHARDT (*Zeit. Ver. deut. Zuckerind.*, 1902, 114—116).—The author has made experiments on the action of animal charcoal extracted with hydrochloric acid and of blood charcoal on inverted solutions of pure sucrose and of sucrose mixed with various proportions of commercial raffinose. In the case of pure inverted sucrose, slight absorption takes place with the extracted animal charcoal, whilst the blood charcoal has a somewhat greater effect. When raffinose is present, however, the lævorotation in some cases undergoes considerable increase, which is greater for the blood charcoal. When less than 2·5 per cent. of raffinose is present, the diminution and increase of the lævorotation due to the absorption of the inversion products of sucrose and raffinose respectively balance one another, but when this proportion is exceeded considerable errors may be made in the analysis, which gives more sucrose and less raffinose than are really present. These results the author considers to be due to the greater absorption of the melibiose formed by the inversion of raffinose.  
T. H. P.

**Testing of Honey.** By WALTER BRAUTIGAM (*Chem. Centr.*, 1902, i, 681—682; from *Pharm. Zeit.*, 47, 109).—The author has found that genuine honey contains a kind of albumin, probably secreted by the bees, as it is also present when these have been fed on cane sugar. The following reactions may serve to distinguish genuine from factitious honey.

Three grams of honey are dissolved in 3 c.c. of water, an equal volume of saturated brine is added, the solution is acidified with acetic acid, and boiled. In genuine samples, a decided separation of albumin is noticed. The albumin obtained from 25 grams of honey after being freed from sodium chloride should dissolve on warming in 4 grams of acetic acid; the liquid becomes turbid on cooling owing to the presence of wax, which, however, dissolves on adding a few drops of chloroform. The filtrate from the albumin is mixed with an excess of ammonia, when on heating to 50° a flocculent precipitate (½ peptone) will appear. (Egg-albumin gives no precipitate, blood-albumin only a slight one.) One-tenth part of this filtrate is mixed with a drop of phenol and heated; there should be no turbidity (absence of blood-albumin). The remainder of the filtrate is mixed with dilute aqueous sodium hydroxide and heated to 50°, when it should remain clear (absence of blood and egg-albumin).  
L. DE K.

**Estimation of Dry Extract in Wines.** By EDWIN ACKERMANN (*Ann. Chim. anal.*, 1902, 7, 87—88).—Ten c.c. or less of the sample are introduced into a weighed platinum dish having a diameter of 5·5 cm. and a height of 1·5 cm., evaporated first on the open water-bath for 20 minutes, and then dried for an hour in a Møeslinger water-oven. The residue is then weighed. If the ash has to be estimated, the dish is placed on an aluminium plate and heated until the mass is charred; if now heated over the naked flame, the carbon will burn with remarkable facility.  
L. DE K.

**Estimation of Potato-Starch (Granulose).** By ALBERT KAISER (*Chem. Zeit.*, 1902, 26, 180).—Fifty c.c. of the 1 per cent. starch solu-



tion, which must be freshly prepared, are mixed with 10 grams of sodium acetate, heated to 50°, and precipitated with a slight excess of iodine solution (5 grams of iodine and 10 grams of potassium iodide in one litre). The precipitate is collected on a weighed filter and washed with a 3 per cent. solution of sodium acetate. After transferring it from the filter into a porcelain dish by aid of a jet of alcohol from a wash-bottle, it is gently heated with 5 c.c. of a 5 per cent. alcoholic solution of potassium hydroxide, which soon decomposes the starch iodide, leaving amorphous starch. The liquid is now rendered decidedly acid by means of an alcoholic solution of acetic acid and the starch collected on the same filter, washed first with hot alcohol, then with absolute alcohol, and finally with ether. After drying for 4 hours at 120°, it is weighed. It should then be tested for any insoluble matter.

L. DE K.

**A New Method for the Estimation of Cellulose.** By SIMON ZEISEL and MILAN JOSEF STRITAR (*Ber.*, 1902, 35, 1252—1255).—About 1—1.5 grams of the finely divided material are mixed with dilute nitric acid and a 3 per cent. aqueous solution of potassium permanganate gradually added to the well-cooled and constantly stirred mixture until a coloration is produced which is permanent after half-an-hour; after removing the excess of permanganate and precipitated manganese dioxide by the aid of sulphurous acid, the residue is thoroughly washed with water, digested with 2½ per cent. ammonia at 60° for  $\frac{3}{4}$  hour, washed with alcohol and ether, and weighed. This method gives results slightly lower than that of Schulze and Henneberg, 37.2 per cent. of cellulose being found in oak-wood, instead of 45.87 per cent.; the product, however, is purer, as shown by the absence of methoxyl groups. Schulze's method, moreover, gives very variable results according to the conditions.

W. A. D.

**Estimation of Acetic Acid in Lead Accumulators.** By CARLO FORMENTI (*Chem. Zeit.*, 1902, 26, 150—151).—Two kilos. of the cut up material are boiled in the water and 50 grams of potassium carbonate; the filtrate is evaporated to dryness and heated for some time at 100°. The potassium acetate is extracted by absolute alcohol, the solution is evaporated to dryness, and the residue again dissolved in alcohol. The potassium acetate is then obtained pure by evaporating the solution in a platinum dish and drying the residue at 100°. After weighing, it may be identified by the cacodyl reaction and other tests for acetates.

L. DE K.

**Detection of Acetoacetic Acid in Urine.** By ED. ALLARD (*Chem. Centr.*, 1902, i, 443; from *Berl. Klin. Wochschr.*, 38, 985—987).—Gerhardt's test will detect the presence of 0.4—0.5 part of acetone in 1000 parts of urine; Arnold's test (*Abstr.*, 1900, ii, 768) shows 0.1 per 1000, and Liplawsky's combination of the above tests will show as little as 0.04 per 1000. For the latter, concentrated ammonia and hydrochloric acid of sp. gr. 1.19 should be used. Both Arnold's and Liplawsky's test (*Abstr.*, 1901, ii, 428) also give a reaction with acetone, a fact of which these authors do not seem to have been aware,

but this is not of much importance, as no acetone reaction is obtained with less than 1 per cent. [ $\frac{1}{1000}$ ]. Of the various reagents for acetoacetic acid, ferric chloride is therefore the only one not affecting acetone.

L. DE K.

**Detection and Estimation of Lactic Acid in Gastric Juice.**  
By ALEXANDER CH. VOURNASOS (*Zeit. angew. Chem.*, 1902, 15, 172—174).—Five c.c. of the gastric juice are filtered and, if the filtrate is slimy, diluted with an equal bulk of water. The solution is rendered alkaline by adding a 10 per cent. solution of potassium hydroxide and boiled for a few minutes, then at once mixed with 1—2 c.c. of a reagent composed of 1 part of iodine, 0.5 of potassium iodide, 5 parts of methylamine, and 50 of water. If lactic acid is present in the proportion of at least 0.005 per cent., a very strong odour of isonitrile will be noticed after some time. Sometimes it is advisable to expel volatile substances and then extract the lactic acid by means of ether before applying the test.

For the quantitative analysis, the following procedure is recommended. Thirty c.c. of the juice are evaporated to 10 c.c. and mixed in a retort with 15 c.c. of aqueous potassium hydroxide and 0.5 gram of iodine; the retort is connected with a properly cooled receiver and the mixture distilled first at a low temperature and finally at 105° until 7/10 of the liquid has passed over. The distillate contains an amount of iodoform corresponding with the quantity of the lactic acid present. It may either be collected on a tared filter, dried at 60°, and weighed, or it may be decomposed with alcoholic potassium hydroxide and the iodine estimated volumetrically with  $N/10$  silver nitrate. 0.1 gram of iodoform corresponds with 0.0229 gram of lactic acid. The liberated iodoform may also be identified by aid of the microscope.

L. DE K.

**Action of Bromine and Potassium Permanganate on Citric Acid (Stahre's Reaction) and Detection of Citric Acid in Milk.**  
By ALFRED WÖHLK (*Zeit. anal. Chem.*, 1902, 41, 77—100).—The highly sensitive reaction for citric acid published by Stahre (*Abstr.*, 1897, ii, 290), namely, the production of a white precipitate, soluble in ether, when bromine and potassium permanganate act on citric acid, does not depend, as was supposed by him, on the bromination of acetone produced by the oxidation of the citric acid. The precipitate consists essentially of pentabromoacetone, if it is formed at the ordinary temperature, although above 45° the principal product is bromoform. Acetone cannot, however, be brominated by bromine water either in diffused daylight or in direct sunlight. Neither is the reaction due to a direct bromination of citric acid, as that acid is recovered unaltered after repeated evaporation with bromine water. The action of an oxidising agent is essential, but manganic acetate, manganic hydroxide, manganese dioxide, ferric, cobaltic, nickelic hydroxides, or lead dioxide can be substituted for the permanganate. The author confirms the production of acetone when citric acid is oxidised by permanganate, but shows that the action takes place in two stages, the first of which corresponds with the formation of acetonedicarboxylic acid. Moreover, Deniges, by his mercuric sulphate test (*Abstr.*, 1900, i, 204), has shown

that acetonedicarboxylic acid is present in the product of the oxidation of citric acid by permanganate, and the author has obtained indications of the presence of a substance of enolic constitution in a solution of citric acid oxidised by a ferric salt in sunlight, by the production of a violet colour with the first portions of bromine added. Now acetonedicarboxylic acid readily yields pentabromoacetone when treated with bromine water at 15°, but at the same time a large part of the acid splits up into acetone and carbon dioxide. Stahre's reaction is therefore not a quantitative one. The test is performed by warming the mixture of citric acid (or a citrate acidified with sulphuric acid) and permanganate to 30—40°, removing any brown colour by addition of ammonium oxalate, and then adding a few drops of bromine water. For Deniges test, which is even more sensitive than Stahre's, although less characteristic, since various ketones, ketonic acids, and aldehydes give a similar result, 5 grams of mercuric oxide are dissolved in 20 c.c. of concentrated sulphuric acid and 100 c.c. of water, one volume of this reagent is added to 20 vols. of the citric acid solution, the mixture heated to boiling, and then a few drops of permanganate are added. A white precipitate is immediately produced.

From 10 litres of cow's milk, the author has obtained several grams of rhombic crystals, which not only gave Stahre's, Deniges, and the ordinary calcium salt reactions, but which, when converted into silver and calcium salts, gave, on elementary analysis, numbers agreeing with those required by citric acid.

M. J. S.

**Estimation of Citric Acid in Milk.** By GEORGES DENIGÈS (*Compt. rend. Soc. Biol.*, 1902, 54, 197—198).—Ten c.c. of milk, 2 c.c. of a 5 per cent. solution of sodium metaphosphate, and 3 c.c. of mercuric sulphate are mixed and filtered. Half the filtrate (about 7.5 c.c.) is mixed with 0.5 c.c. of a 10 per cent. solution of manganese sulphate and boiled. To this, 4 drops of a 2 per cent. solution of potassium permanganate are added and the mixture again boiled; this is repeated, and the fluid decolorised by a drop of hydrogen peroxide; an opalescence or a precipitate indicates the presence of citric acid. For quantitative purposes, the depth of the opalescence is compared with that in standard tubes previously prepared.

W. D. H.

**Decrease in the Acidity of Milk.** By ARTHUR KIRSTEN (*Zeit. Nahr.-Genussm.*, 1902, 5, 97—109).—Many experiments are described showing that the acidity of milk decreases when the milk is kept in open vessels; also when it is boiled or subjected to centrifugal action. This is due to a partial loss of the carbon dioxide dissolved in the milk. It is further pointed out that the acidity of fresh milk is not alone due to acid phosphates, but in part to dissolved carbon dioxide.

The so-called "incubation stage" of milk, discovered by Soxhlet, until now defined as the period during which the acidity of milk remains constant in spite of the increase of acid-producing bacteria, is better described, in the light of the author's experiments, as that period in which the lactic acid bacteria produce only as much lactic acid as is balanced by the loss of free carbon dioxide. During the "incubation stage," the acidity may even decrease.

W. P. S.

**"Butter Oil."** By F. UTZ (*Zeit. öffentl. Chem.*, 1902, 8, 48—49).—A sample of cooking oil sold in Germany under the name of "butter-oil" was found to consist entirely of cottonseed oil. An article imported from America as "cooking fat" was found to be a mixture of 95 per cent. of cottonseed stearin with 5 per cent. of beef stearin. Another substance—nut butter—was simply a mixture of earthenut meal and earthenut oil. W. P. S.

**Analysis of Turkey-Red Oil.** By W. HERBIG (*Chem. Rev. Fett. Harz. Ind.*, 1902, 9, 5—8).—The combined sulphuric acid is estimated by boiling 4 grams of the sample with 30 c.c. of dilute hydrochloric acid (1 : 5) for about 40 minutes in a reflux apparatus; it is necessary to shake the mixture frequently. Both the acid and fatty layer should be quite clear, and when cold the latter is dissolved by addition of ether. The whole is now introduced into a separating funnel, the acid layer is drawn off, and the ethereal layer freed from any acidity by shaking three times with a little water. After expelling the ether from the acid solution, this is, as usual, precipitated with barium chloride. The total fatty matter is estimated by heating 30 grams of the sample with 100 c.c. of water and adding 25 c.c. of dilute sulphuric acid. To the mixture, which is contained in a 200 c.c. flask having a long neck graduated to 0.1 c.c., is then added hot brine until the fatty mass has collected in the neck. After half-an-hour its volume is read off, and in calculating this to weight, its sp. gr. may be assumed to be 0.945.

It appears that when boiled with dilute acids triglycerides lose part of the glycerol. To what extent this affects the analysis of turkey-red oil will be the subject of a further investigation. L. DE K.

**Halphen's Reaction.** By A. STEINMANN (*Ann. Chim. anal.*, 1902, 7, 85—87).—Many inconveniences experienced when applying Halphen's reaction may be avoided by the simple plan of heating the mixture of the oil with amyl alcohol and solution of sulphur in carbon disulphide in a sealed tube. The tube is partly filled by the well-known device of warming it and dipping the drawn-out end into the mixture; the point is then sealed. There is very little risk of the tube breaking if it is put into cold water, which is then gradually heated to boiling. A tube fitted with a tied-down glass stopper may also be used.

L. DE K.

**The Chemistry of Halphen's Reaction for Cottonseed Oil.** By PAUL N. RAIKOW (*Chem. Zeit.*, 1902, 26, 10—11).—It is known that cottonseed oil mixed with sulphur and exposed for a long time to sunlight becomes indifferent towards Halphen's reagent. The author has noticed that exposure to sunlight alone will gradually diminish the quantity of the active substance causing the reaction; slight traces of added sulphur have no sensible effect. L. DE K.

**Estimation of Fat in Bread and Determination of the Nature of the Fat.** By T. C. BERNTRUP (*Zeit. angew. Chem.*, 1902, 15, 121—125).—One hundred and fifty grams, or more, of the sample are boiled in a reflux apparatus with 500 c.c. of water and 100 c.c. of hydro-

chloric acid for 2 hours over the naked flame. (When testing flour, the mixture should be heated first for one hour in the boiling water-bath.) When cold, the insoluble matter is collected on a filter, washed with cold water until the acidity is removed, and then dried for an hour at 100—110°. The mass, which can be readily detached from the filter is reduced to powder in a mortar with addition of some sand, the paper cut into small pieces, and the whole introduced into a fat-free paper cartridge and extracted in a special apparatus for one hour with ether, light petroleum, or carbon tetrachloride. The apparatus consists of a flat bottomed, cylindrical boiling flask, 4 cm. wide and 11.5 cm. high, having a ground neck connected with an open cylinder, the top of which is fitted with a perforated cork through which passes the condensing tube. By means of two strings fitted to it, the cartridge may be pulled up so that the contents may be extracted for the first half hour when actually in contact with the boiling liquid contained in the flask. Experiments are communicated to show that the extraction of the fat is complete, and that previous ideas about fat disappearing during the baking process were solely due to the fact that the old extraction processes used in the case of bread were untrustworthy. The process may also be applied to the analysis of condensed milk.

The fat contained in wheaten flour averages 1.68 per cent.; any large excess, therefore, points to added fatty matter. To see whether this is due to the use of milk, the Reichert-Meissl number of the extracted fat should be taken. Pure wheaten flour fat has a Reichert-Meissl figure of 1.8; a lower figure points to the presence of fats of the margarine type. When calculating the results obtained with bread, it may be assumed that 100 parts of dry bread contain 90 parts of dry flour.

L. DE K.

**Methods of estimating Fat in Fodders.** By C. BEGER (*Chem. Zeit.*, 1902, 26, 112—113).—The author is of opinion that in accurate scientific work the fatty matter should be rendered accessible to solvents by removing any albuminous matters by Dormeyer's pepsin process. Three or five grams of the substance are digested with 480 c.c. of water and 20 c.c. of 25 per cent. hydrochloric acid for 24 hours at 37—40° after adding 1 gram of Merck's pepsin. Both residue and liquid are then extracted with ether. A number of cases are given showing the value of the method. One sample of gluten which gave 0.85 per cent. of fat by the ordinary Soxhlet treatment yielded 5.74 per cent. by the pepsin process.

L. DE K.

**Rapid Detection of Formaldehyde in Foods.** By CARL ARNOLD and CURT MENTZEL (*Chem. Zeit.* 1902, 26, 246—247).—The following test may be applied directly to liquid foods or an aqueous or alcoholic extract of solid foods.

In 3—5 c.c. of the liquid (milk, for instance) is dissolved a lump of phenylhydrazine hydrochloride the size of a pea, 2—4 drops of a 5—10 per cent. solution of sodium nitroprusside are added, and finally 8—12 drops of 10—15 per cent. sodium hydroxide. In the presence of even traces of formaldehyde, a fairly permanent blue or bluish-green

colour is produced. The test is rendered still more delicate by substituting potassium ferricyanide for the nitroprusside, but it cannot then be recommended for milk or meat preparations containing blood-colouring matter; in case of an alcoholic solution, this must be well diluted with water to prevent precipitation of potassium ferricyanide.

L. DE K.

**Method for the Detection of Glucosamine and its Employment on the Decomposition Products of Mucin.** By H. STEUDEL (*Zeit. physiol. Chem.* 1902, 34, 353—384).—See this vol., i, 399.

**Occurrence and Detection of Berberine in Plants.** By HARRY M. GORDIN (*Arch. Pharm.*, 1902, 240, 146—149).—It has been customary to add excess of hydrochloric acid to the aqueous or alcoholic extract of the plant, and, if a yellow precipitate is produced the solution of which in water is reddened by chlorine water, to conclude that berberine is present. This method is untrustworthy.

The powdered drug (5—20 grams) should be extracted with hot alcohol, the extract evaporated, the residue diluted with 20—40 c.c. of water, filtered (after the addition of a little powdered talc, if necessary), and a few c.c. of the clear filtrate mixed with 10 per cent. potassium iodide solution. If no precipitate is formed, no appreciable quantity of berberine is present. If a precipitate forms, 10 c.c. of the original clear filtrate are mixed with 1 or 2 c.c. of 10 per cent. aqueous sodium hydroxide, filtered if necessary, heated to 50°, mixed with 5 c.c. of acetone, and set aside. If no crystals of berberine-acetone have appeared after 2 hours, 30 c.c. of water are added, and the whole is left overnight in a cool place. Crystals will separate if not less than 0.01 gram of berberine was present in the original 10 c.c. They may be identified by washing them with water, dissolving them in very dilute hydrochloric acid, and testing portions of the solution with potassium iodide, potassium dichromate, picric acid, and chlorine water.

*Berberis vulgaris* and *B. Aquifolium*, *Hydrastis canadensis*, *Xanthorrhiza aquifolia*, and *Coptis trifolia* contain berberine; *Cocculus palmatus*, *Pareira brava*, *Menispermum canadense*, and *Jeffersonia diphylla* do not.

C. F. B.

**Behaviour of Morphine and Strychnine in Putrefying Corpses.** By WILHELM AUTENRIETH (*Chem. Centr.*, 1902, i, 376—377; from *Ber. Deutsch. pharm. Gesel.*, ii, 494—502).—Morphine is but little affected by the putrefaction process, but strychnine is partially decomposed, or at least so altered that the products give no reaction with sulphuric acid and potassium dichromate. For the detection of morphine or strychnine, the author uses the Stas-Otto process, substituting, however, hot chloroform for amyl alcohol; when testing urine, this is acidified with tartaric acid and first evaporated to a syrup. If the alkaloidal residue looks greasy, it is dissolved in water containing 1 per cent. of hydrochloric acid, and the filtered liquid is then rendered alkaline and agitated with ether to dissolve the alkaloid.

In acute opium poisoning, the meconic acid passes unchanged into

the urine. In a sample of urine which had been exposed for 15 months, the alkaloid could still be detected, but no reaction could be obtained for meconic acid.

L. DE K.

**Analysis of Rubber Wares.** By ARVID HEINTZ (*Chem. Zeit.*, 1902, 26, 247—248).—The various matters added to rubber, such as fats, asphalt, "factis," &c., are removed by means of suitable solvents, alcoholic potassium hydroxide, ether, nitrobenzene, &c. The residue is then sharply dried and an aliquot part is burnt with lead chromate in a combustion tube. From the weight of the water formed the quantity of true rubber may be calculated, assuming it to consist of a hydrocarbon,  $C_{10}H_{16}$ .

L. DE K.

**New Reagent for the Detection of Albumin in Urine.** By EGIDIO POLLACCI (*Chem. Centr.*, 1902, i, 224—225; from *Boll. Chim. Farm.*, 40, 789—791).—A modification of Spiegler's test. One gram of tartaric acid, 5 grams of mercuric chloride, and 10 grams of sodium chloride are dissolved in 100 c.c. of water, filtered, and mixed with 5 c.c. of 40 per cent. formaldehyde. The test is made by carefully pouring 3—4 c.c. of the urine on to 2 c.c. of the reagent. An immediate white ring forming at the place of contact shows pathological albumin, but the reaction is so delicate that even in normal urines a slight ring generally shows after 8—15 minutes. A table is given showing the comparative delicacy of this and several other reagents. One part of albumin may be detected in 370,000 parts of solution; the nitric acid (Heller) test only shows one in 78,000.

L. DE K.

**Solution and Estimation of Coagulated Proteids by Thiosinamine.** By OEFELE (*Chem. Centr.*, 1902, i, 502; from *Pharm. Centr.-Halle*, 43, 1—4).—The author has found that thiosinamine dissolves coagulated albumin and uses this reaction for the isolation of proteids in fæces. A portion of the sample is mixed to a paste with sand, thiosinamine, and a little water, and digested on the water-bath. The mass is then thrown on to a filter and repeatedly extracted with boiling water; the filtrate contains the proteids, the thiosinamine, and a number of substances soluble in alcohol. The proteids may be removed by means of picric acid or the solution after being concentrated is repeatedly precipitated with excess of absolute alcohol. The normal quantity of coagulated proteids soluble in thiosinamine contained in fæces amounts to 4—8 per cent.

L. DE K.

**Analysis of Meat Extracts and Vegetable Extracts.** By KARL MICKO (*Zeit. Nahr.-Genussm.*, 1902, 5, 193—201).—The results of the analyses of various meat and vegetable extracts are given, the usual methods being employed for the separation of the different constituents. The amounts of creatine (or creatinine respectively) and of xanthine bases contained in the extracts are also given. For the estimation of the creatine, from 5 to 20 grams of the extract are boiled with 100 c.c. of water and 10 c.c. of dilute sulphuric acid (1 : 3) for 3

hours under a reflux condenser. The liquid is then neutralised with sodium hydroxide, the xanthine bases are precipitated with sodium hydrogen sulphite and copper sulphate, and filtered off. The excess of copper is removed from the filtrate as sulphide and the filtrate evaporated to a syrupy consistency. The residue so obtained is thoroughly extracted with boiling alcohol, the alcoholic solution evaporated to about 300 c.c., neutralised with alcoholic sodium hydroxide, filtered, and precipitated by the addition of 0.5 c.c. of a concentrated alcoholic solution of zinc chloride. The precipitate of creatinine-zinc chloride which forms is collected, as is also a further quantity obtained on concentrating the solution to about 40 c.c. The nitrogen in the precipitates is then estimated by Kjeldahl's method. Approximately 6 per cent. of creatine was found in Liebig's extract.

The xanthine bases may be determined by dissolving 10 grams of the extract in 100—200 c.c. of boiling water and precipitating by adding 40 c.c. each of saturated sodium hydrogen sulphite solution and a 13 per cent. solution of copper sulphate. After remaining overnight, the precipitate is collected, washed with previously boiled cold water, and boiled with a little water acidified with hydrochloric acid. The copper is then removed as sulphide and the cold solution precipitated with silver nitrate solution in the presence of excess of ammonium hydroxide. After 12 hours, the precipitate is collected, washed with dilute ammonia, then with water, and brought into a flask, where, after the addition of hydrochloric acid, the silver is removed as sulphide. The filtrate from the silver sulphide is concentrated by evaporation and reprecipitated with silver nitrate. The precipitate obtained is washed completely with water, then with alcohol, and the nitrogen it contains estimated. The filtrate from the copper hydrogen sulphite precipitate still contains a small quantity of xanthine bases. These may be estimated, after removal of the copper, by precipitation with silver nitrate as above, the amount of nitrogen found being added to the first quantity. Liebig's extract contained an average of 0.648 per cent. of nitrogen as xanthine bases; "Sitogen" (yeast extract), 0.637 per cent. Whether the nitrogen in the silver precipitate exists solely as xanthine bases has not yet been determined, nor is it known whether the latter are identical in both meat and vegetable extracts.

W. P. S.

**Alkalimetric Estimation of Disodium Methylarsenate (Arrhenal).** By A. ASRRUC (*Compt. rend.*, 1902, 134, 660—661).—The salt  $\text{Na}_2\text{AsMeO}_3 \cdot 5\text{H}_2\text{O}$  is neutral to Poirrier's blue, but alkaline to litmus, rosolic acid, phenolphthalein, or helianthin-A.

On titrating the aqueous solution with a mineral acid, neutrality is attained in the presence of litmus or rosolic acid by the employment of 1 equivalent of the reagent, the end points being especially distinct in the case of the latter indicator. Under these conditions, the solution remains alkaline to helianthin-A until  $1\frac{1}{2}$  to 2 equivalents of acid are added, but in this case the end point is ill-defined, and a similar result is obtained with phenolphthalein (compare Abstr., 1901, ii, 144).

G. T. M.



**Analysis of the Apple and some of its Products.** By C. A. BROWNE (*J. Amer. Chem. Soc.*, 1901, 23, 869—884).—*Moisture*.—As lævulose and other substances cannot be dried at 100° without suffering decomposition and loss in weight, the author mixes the pulp or the juice of the apple with asbestos contained in a perforated copper tube and dries at 70° for 8 or 10 hours in "a vacuum of about 25 inches." During the first few hours of the drying, a slight air-current is passed to more readily remove the excess of moisture. The percentage of solid matter in unfermented apple juices may also be determined in a sufficiently accurate manner by using the formula  $245(S-1)$ , in which  $S$  represents the sp. gr. of the juice at 17.5°. *Ash*.—This is determined in the usual way, the charred mass being exhausted with water before being completely burned; the aqueous solution is evaporated separately. *Reducing sugar*.—One hundred grams of the grated pulp are repeatedly washed on a muslin filter with cold water, the filter being each time squeezed to hasten the removal of the sugar. The washing is continued until nearly two litres of liquid are collected; after carefully making up to the mark and shaking, 200 c.c. of the filtered liquid are transferred to a 250 c.c. flask, neutralised with sodium hydroxide, using phenolphthalein as indicator, and diluted to the mark. Twenty-five c.c. of this solution (1 gram of apple) are then used for the estimation; the cuprous oxide is reduced as usual by hydrogen, and the metallic copper weighed. *Sucrose*.—This is estimated by the increase in cupric reducing power after heating the solution for 5 minutes at 70° with addition of 10 per cent. by volume of fuming hydrochloric acid. It may also be determined by polariscopic observation before and after inversion. *Lævulose and dextrose*.—These may be calculated from the rotation and cupric reducing power of the solution, advantage being taken of the fact that on raising the temperature lævulose gradually loses its polarising power. *Starch*.—The liquid prepared for the estimation of the reducing sugars contains in suspension the starch which gradually deposits, and may then be washed by decantation. After finally washing it on a hardened filter, it may be dissolved by means of diastase, inverted by hydrochloric acid, and determined by the copper process. *Marc*.—This is the insoluble part of the fruit. The residue left on the muslin filter is transferred to a dish and dried at 100°. With the exception of a trace of ash, it is almost wholly composed of cellulose, lignin, and pentosans. The last named may be estimated as usual by conversion into furfuraldehyde, and precipitating this by phloroglucinol; cellulose may be estimated by Cross and Bevan's chlorination process, lignin being found by difference. *Malic and acetic acids*.—Malic acid is found by titration with  $N/10$  soda, combined acid being calculated from the alkalinity of the ash. In the case of ciders and vinegars, the acetic acid may be determined separately by distillation in a current of steam and subsequent titration; the residue is then titrated for malic acid. *Pectin*.—A definite volume of the extract or juice is evaporated to a small volume and precipitated with excess of alcohol. The precipitate is afterwards collected in a Gooch crucible, washed with alcohol, dried at 100°, and weighed. It is then burnt and any ash allowed for. Tables are given showing the average composition of the flesh of the ripe apple,

the composition of apple ash, apple juices, ciders, vinegars, other apple products and other fruits for comparison. L. DE K.

**Cocoa-Shell Powder.** By PAUL WELMANS (*Zeit. öffentl. Chem.*, 1901, 7, 491—500).—The results are given of a number of determinations of the amounts of shell or husk obtained from raw and roasted cocoa beans. On the raw beans, the quantity varied from 8·00 to 17·72 per cent., with an average of 13·30 per cent., and on the roasted beans from 9·60 to 16·00 per cent., the average being 12·40 per cent. Analyses are also given of various samples of cocoa powder. As regards the estimation of the quantity of added cocoa-shell powder in cocoas, the author recommends the determination of the percentage of ash; the iodine number and acidity of the fat obtained from the sample; the amount of cold water extract; the crude fibre, and the pentosans. The fat in cocoa-shell powder is about 7·5 per cent., having 35·3° of acidity (Burstyn degrees). The iodine number of the fat is about 45 per cent. The cold water extract averages 24·6 per cent., and the ash, 8·60 per cent. The average percentage of crude fibre in the shell powder is 12·3. The percentage of pentosans (as determined by the phloroglucinol method) gives the best indication of admixture as the quantity present in cocoa-shell powder is about 8·5 per cent., whilst ordinary Dutch cocoa contains approximately 2 per cent. W. P. S.

**Oats-Cocoa.** By R. PETERS (*Chem. Centr.*, 1902, i, 332—333; from *Pharm. Centr.-Halle*, 1901, 42, 819—828).—Oats-cocoa consists of a mixture of 33·5—60 per cent. of cocoa powder, freed from oil, with 40—60 per cent. of prepared, or more usually ordinary, oatmeal, and in some cases small quantities of nutritive salts are also present.

The percentages of cocoa powder and oatmeal may be determined as follows. The sample is examined microscopically to ascertain whether it consists of a mixture of oatmeal and cocoa only. The fat is then extracted, weighed, and its iodine number determined. Assuming the iodine number of oil of oats to be 98, and that of cocoa butter 36, the proportion of these materials in the fat may be calculated, and since oatmeal contains on an average 6 per cent. of oil, the percentage of oatmeal in the original powder is readily found. The cocoa powder is estimated by difference.

The extracted fat should be tested for the presence of adulterative fat which would have an iodine number less than 36. If cocoa butter has been added the fat would give an extraordinarily low iodine number, and in this case the ash should be determined. The quantity of cocoa powder may then be calculated from the average percentages of ash yielded by oatmeal and cocoa powder respectively. If the value thus obtained is considerably less than that calculated from the iodine number, then cocoa butter has doubtless been added. In the original paper, a table is given showing the maximum iodine numbers of the fats extracted from oats-cocoas containing 33½, 40, 50, and 60 per cent. of cocoa powder respectively. In the case of samples which contain other components, the quantity of oatmeal is found as before, but that of the cocoa powder is estimated by assuming that it contains 27 per cent. of fat. E. W. W.

## General and Physical Chemistry.

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**Indices of Refraction of Mixed Liquids.** By EDMOND VAN AUBEL (*Compt. rend.*, 1902, 134, 985—987).—The author has examined the relationship developed by Leduc (*Compt. rend.*, 1902, 134, 645):  $(N-1)U = m(n-1)u + (1-m)(n'-1)u'$ , where  $m$  is the weight of one of the constituents,  $u$ ,  $u'$ , and  $U$  are the specific volumes of the constituents and mixture respectively, and  $n$ ,  $n'$ , and  $N$  their refractive indices. The formula gives good results for mixtures of acetone and water (Drude, Abstr., 1897, ii, 438) and aniline and ethyl alcohol (Johst, *Ann. Phys. Chem.*, 1883, [ii], 20, 9). It is shown that the value of  $(n-1)/d$  is not constant for various mixtures.

J. McC.

**Maxwell's Law,  $n^2 = K$ , for some Compounds containing Nitrogen.** By EDMOND VAN AUBEL (*Compt. rend.*, 1902, 134, 1050—1052).—In the case of nitro-compounds, nitrates, amines, and nitriles, Maxwell's law connecting the refractive index with the dielectric constant is not valid. With these substances, the dielectric constant diminishes as the molecular weight rises whilst the refractive index increases.

J. McC.

**Lamps for Spectra. IV.** By ERNST BECKMANN (*Zeit. physikal. Chem.*, 1902, 40, 465—474. Compare Abstr., 1900, ii, 701; 1901, ii, 53, 81).—In order to prevent solid particles of material used in the production of coloured flames from coming into the air, the burned gas should be aspirated by a falling current of water into the bottom of a vessel the upper part of which contains fat-free cotton wool. Washing with water is not sufficient to remove these solid particles. With the Morton form of sprayer, a good coloured flame can be obtained; the air-blast, carrying the solid, enters into a chamber, from which it passes to the burner.

A simple lamp, suitable for chemical laboratories, is made by attaching a right-angled sprayer to a wide tube which contains a drop-collector and is connected with the bottom of an ordinary metal burner. The gas pressure may be conveniently obtained from a cylinder of compressed air or oxygen.

J. McC.

**Band Spectra of Nitrogen.** By HENRI DESLANDRES (*Compt. rend.*, 1902, 134, 747—750).—It is shown that the expression  $N = 22785 \cdot 1 - \frac{30 \cdot 318}{8}(2n)^2 + \frac{29 \cdot 363}{8}(2p+1)^2$ , where  $n$  and  $p$  vary by successive additions of unity, accurately gives the position of the whole 42 bands of the first group of bands in the spectrum of nitrogen (Compare Cuthbertson, *Phil. Mag.*, 1902, [vi], 3, 348).

L. M. J.

**Some New Peculiarities in the Structure of the Cyanogen Bands.** By ARTHUR SCOTT KING (*Ann. Physik.*, 1902, [iv], 7, 791—800).—An investigation of the arc light spectrum, dealing

specially with a series of bands in the ultra-violet which have not been described by previous workers. The author regards the band structure referred to as the "tails" of the cyanogen bands; the new bands are affected by change of the atmosphere surrounding the arc in the same way as the edges of the cyanogen bands. The influence of atmospheres of carbon dioxide, nitrogen, and oxygen on the character of the carbon bands and the cyanogen bands is described. The carbon used in the investigation was prepared by ignition of pure sucrose.

J. C. P.

**Ultra-violet Absorption Spectra.** By G. PAUL DROSSBACH (*Ber.*, 1902, 35, 1486—1489. Compare this vol., ii, 190).—The author has extended his observations to salts of the rare earths and to several organic liquids. Using the same notation (*loc. cit.*) to represent ultra-violet absorption, it is found that methyl and ethyl alcohol are completely transparent, whilst the higher alcohols have a more or less extensive absorption; propyl alcohol, 290; isobutyl alcohol, 335; amyl alcohol, 332; allyl alcohol, 310. The presence of traces of the higher alcohols in ethyl alcohol can be detected by this means. In the case of the aromatic hydrocarbons, the absorption by benzene is represented by 290; toluene, 288; xylene, 310; *m*-xylene, 307; mesitylene, 336. The ultra-violet absorption very clearly distinguishes between the erbium and didymium groups of elements.

Exner's results are discussed and criticised.

K. J. P. O.

**Radioactivity and the Electron Theory.** By SIR WILLIAM CROOKES (*Proc. Roy. Soc.*, 1902, 69, 413—422).—That electrons (or "radiant matter") emanating from radioactive substances behave like material particles is shown by a series of experiments with actinium, radium, and polonium. The emanations from the last-named diffuse much less readily through air than do those from actinium and radium. The corpuscles from radium and actinium may be carried through a tube by a current of air, but this behaviour is not shown by the emanations from hydrogen peroxide.

J. C. P.

**Stratifications of Hydrogen.** By SIR WILLIAM CROOKES (*Proc. Roy. Soc.*, 1902, 69, 399—413).—When a tube provided with aluminium terminals and containing hydrogen is exhausted to 4 mm. by means of a mercury pump, the strata, or "buttons," observed on the passing of a discharge are blue on the convex side facing the negative pole, and pink on the other side. Spectroscopic examination shows strong hydrogen lines in the pink parts, and both hydrogen and mercury in the blue parts. When the exhaustion is raised to 2 mm., the blue is concentrated in one well-formed "button" nearest the negative pole, all the others remaining pink; on the blue "button," mercury alone can be detected, on the pink portions, hydrogen (chiefly) and mercury. At 1 mm., scarcely any hydrogen can be detected, the stratifications have almost disappeared, and mercury is strong all through the tube. Hydrogen strata showing no blue have been obtained by interposing between the vacuum tube and the mercury pump either (1) tubes containing copper, sulphur, and iodine, or (2) a glass spiral

immersed in ice-water. Occasionally, when no mercury was present, the author observed a faint blue edging on some of the pink strata; this was traced to an impurity in the phosphoric oxide used; this phosphoric blue, however, is much paler than the mercury blue. The blue colour of the strata in a tube containing both mercury and hydrogen may be eliminated also by introducing a water resistance, and thus altering the intensity of the spark.

It is very difficult to obtain stratification in mercury vapour, and the above observations show that the presence of hydrogen facilitates such stratification; the hydrogen strata probably act as obstructions in the same manner as a constriction in the tube or sealed-in wires. The pink and blue luminosities show where the electrons and gaseous atoms meet, the dense mercury atom not being driven back so much as the lighter hydrogen atom.

J. C. P.

**Some Measurements with Gas Elements.** By EMIL BOSE (*Zeit. anorg. Chem.*, 1902, 30, 406—408. Compare Abstr., 1900, ii, 704; 1901, ii, 589).—A discussion of some points raised by Czepinski's paper (this vol., ii, 298). In particular, the author lays stress on his view that the hydrogen-oxygen cell is perfectly reversible.

J. C. P.

**Elements founded on the Reciprocal Action of Oxidising and Reducing Liquids. Common Solvents. Action of Acids and Bases.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1902, 134, 933—950. Compare following abstract).—In order to ascertain the mechanism of the production of free acid in animal secretions, the *E.M.F.* of various cells has been determined, and the same after the addition of an oxidising agent to one pole, of a reducing agent to the other pole, and of both additions simultaneously. The following concentration cells were examined: hydrochloric acid, sulphuric acid, lactic acid, oxalic acid, and formic acid. A reducing agent (pyrogallol) added to the liquid at the + pole hardly alters the *E.M.F.*, but when added to the liquid at the - pole the *E.M.F.* increases. An oxidising agent (hydrogen peroxide) at either pole increases the *E.M.F.* From the results obtained, it is concluded that acids are not favourable for the production of a sufficient *E.M.F.* to cause external electrolysis. Much better results are obtained with cells containing alkalis, of which the following were investigated: sodium hydroxide, sodium hydrogen carbonate, sodium formate, and ammonia. In these cases, pyrogallol, formaldehyde, and dextrose were used as reducing agents, and hydrogen peroxide as oxidiser. Using 0.2*N* sodium hydroxide and formaldehyde in the interior vessel, four elements suffice to electrolyse acidified water and to decompose an aqueous solution of sodium sulphate. Using different concentrations of sodium chloride, even addition of pyrogallol does not cause sufficient *E.M.F.* to produce electrolysis when 24 cells are employed. In neutralisation elements, the *E.M.F.* is greatly increased by the addition of a reducing or oxidising agent; this has been shown to be the case with elements constituted of: sodium hydroxide and sulphuric acid; sodium hydroxide and hydrochloric acid; sodium hydroxide and oxalic acid; sodium

hydroxide and acetic acid ; sodium hydroxide and lactic acid ; sodium hydroxide and nitric acid (the results in this case are analogous to the others, proving that the oxidising action of the nitric acid exerts scarcely any disturbing influence) ; sodium hydroxide and formic acid ; and ammonia and hydrochloric acid (in this case, pyrogallol produces a very great increase in the *E.M.F.*, but formaldehyde scarcely affects it). J. McC.

**Elements founded on the Co-operation of a Reaction between Salts with the Reciprocal Action of Oxidising and Reducing Liquids.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1902, 134, 1009—1030. Compare preceding abstract).—The influence of the addition of oxidising and reducing agents on the *E.M.F.* of cells containing a free acid opposed to its normal salt has been investigated. With sodium sulphate and sulphuric acid, the voltage is increased by the addition of pyrogallol to the salt solution, and still further when hydrogen peroxide is simultaneously added to the acid. Hydrogen peroxide added to the acid alone diminishes the voltage. Addition of the same oxidising or reducing agent to both solutions causes an inversion of the poles and a decrease of *E.M.F.* on account of polarisation. Electrolysis can be carried out with 12 elements, containing pyrogallol in the salt solution and hydrogen peroxide in the acid. Similar results have been obtained with sodium oxalate and oxalic acid, lactates, acetates, chlorides, nitrates, formates, and also with ammonium chloride and hydrochloric acid.

Quite analogous results are obtained by the examination of cells containing sodium hydroxide opposed to sodium chloride, sulphate, nitrate, acetate, oxalate, lactate, or formate, and with ammonia opposed to ammonium chloride. The production of electrolysis is greatly favoured by the presence of alkali, and by the action of pyrogallol.

When pyrogallol is added to the sodium hydrogen carbonate of a cell containing this opposed to lactic acid, electrolysis can be carried out ; the voltage rises from 0.20 before the addition to 0.42 volt after the addition. By adding at the same time hydrogen peroxide to the acid, the *E.M.F.* rises to 0.58 volt. The effect of reducing agents (pyrogallol, formaldehyde, and dextrose) on the *E.M.F.* of this cell and others consisting of sodium hydrogen carbonate opposed to oxalic and formic acids and sodium formate opposed to lactic acid has been studied.

In the theoretical discussion, the author points out that the special conditions in a cell essential for external electrolysis depend on (1) the energy furnished in a given time by the chemical reactions taking place in the cell, and (2) the energy dissipated on external electrolysis and other outside circumstances. The energy furnished in a given time is determined by the velocity of the reactions, and this is conditioned by three factors: (1) purely chemical, (2) electrolytic, and (3) physical. These points are discussed in their bearing on the results just described, due account being taken of the conductivities. The reactions treated of are important in the electrolysis of organic compounds, and may be used to explain certain physiological changes.

J. McC.

**Increase of Electrical Resistivity caused by Alloying Iron with various Elements, and the Specific Heat of those Elements.** By W. FLETCHER BARRETT (*Proc. Roy. Soc.*, 1902, 69, 480—485).—When iron is alloyed with tungsten, cobalt, nickel, chromium, carbon, manganese, silicon, or aluminium, there is a decrease in conductivity, but this decrease has apparently no connection with the conductivity of the added element; thus aluminium, which is a much better conductor than nickel, has a far greater effect than the latter metal on the conductivity of iron. The author finds that the elements with the highest atomic weight produce the least increase in the resistance of iron. It is further shown that the order of magnitude of this increase is nearly the same as the order of the specific heats of the added elements. The order of thermal conductivity of the alloys has so far been found to be the same as the order of electrical conductivity. The order of magnetic permeability of the alloys is quite different from that of their electrical conductivity. The magnetic susceptibility of iron is increased by the addition of silicon and especially of aluminium, probably owing to the affinity of these elements for oxygen.

J. C. P.

**Permeability of Animal Membranes.** By G. GALEOTTI (*Zeit. physikal. Chem.*, 1902, 40, 481—497).—The resistance offered to the passage of an electric current in a specially constructed cell by 0.1*N* and 0.8*N* solutions of sodium chloride, sodium fluoride, potassium chloride, ammonium chloride, sodium sulphate, potassium oxalate, ammonium sulphate, calcium chloride, and magnesium sulphate was determined by the Kohlrausch method. The following animal membranes were then introduced on a silver ring into the cell, and the resistance again determined: intestine of sheep, pericardium of dog, mesentery of young dog, bladder of turtle, cæcum of dog, and intestine of holothurium. The membranes were used fresh, and after being killed by chloroform vapour. The intestine of sheep and the mesentery of dog are easily permeable by the ions, and the resistance is not much increased by the introduction of these into the cell. The pericardium of dog is easily permeable by the univalent ions of a binary electrolyte, but the bivalent ions do not pass through so easily. Introduction of the turtle bladder greatly increases the resistance, and the ions, therefore, do not pass through easily. The behaviour of the cæcum of dog and intestine of holothurium shows that the sodium ion passes through more easily when present with the chlorine ion than when with the fluorine ion; the chlorine ion permeates more easily when associated with the sodium ion than when with ammonium, calcium, or potassium ions;  $\text{SO}_4^{--}$  passes through more easily when derived from magnesium sulphate than when it is the product of dissociation of sodium or ammonium sulphate.

The permeability of the first three membranes mentioned is hardly affected by killing, and so these are to be regarded simply as diffusion membranes. The permeability of the other membranes is greatly increased by killing, so that the resistance observed with the dead membrane in the cell is almost the same as that without a membrane.

J. McC.

**Thermostats and Thermoregulators.** By WILLIAM C. GEER (*J. Physical Chem.*, 1902, 6, 85—105).—The author first briefly discusses the various forms of thermostats, namely, those dependent on the equilibrium of two different phases, and those dependent on mechanical regulators. The essentials of a good thermostat are (1) good insulation and low radiation constant; (2) delicate control of heat supply; (3) thorough stirring; (4) simple and sensitive regulation. He then describes a form of thermostat by which with ease constancy to  $0.005^{\circ}$  is obtained, and with care, a much higher constancy. The water-bath is heated by an electric current which passes through a lamp resistance, or may be short circuited. When the temperature falls, the current is short circuited, but when it rises it causes the closing of a relay circuit by which the lamp resistance is again thrown into the heating circuit. L. M. J.

**A Thermostat Sensitive to a Thousandth of a Degree.** By WALTER P. BRADLEY and A. W. BROWNE (*J. Physical Chem.*, 1902, 6, 118—135).—The thermostat was one employed in the determination of critical constants, and consists of two main parts, (1) the thermostat proper, and (2) the reservoir containing water kept at an approximately constant temperature a little above that of the thermostat. The water in this reservoir feeds the thermostat, but the supply is throttled by mercury, and if necessary cut off. The throttling is, however, preferable, as directly the cut off occurs the temperature becomes oscillatory, whereas when it is within the throttling range it is almost absolutely constant. L. M. J.

**Specific Heat of Substances at the Absolute Zero.** By A. PONSOT (*Compt. rend.*, 1902, 134, 703—705).—The author deduces by thermodynamical reasoning the following: (1) at absolute zero, the heat thermal capacity of a system is the sum of the thermal capacities of its elemental components in the solid state. (2) The specific heat of a saturated vapour is less than that of its solid or liquid, but both tend towards the same value at absolute zero (compare Behn, *Abstr.*, 1900, ii, 259). L. M. J.

**Boiling Point of Selenium and other Pyrometric Constants.** By DANIEL BERTHELOT (*Compt. rend.*, 1902, 134, 705—708).—The following values have been obtained by the author by means of an apparatus previously described (*Compt. rend.*, 1895, 120, 831; 1898, 126, 410). Boiling point of selenium,  $690^{\circ} + (h - 760)/10$ ; where  $h$  is the pressure in millimetres not far removed from the normal pressure; boiling point of cadmium,  $778^{\circ} + (h - 760)/9$ ; boiling point of zinc,  $918^{\circ} + (h - 760)/8$ ; melting point of silver,  $962^{\circ}$ ; melting point of gold,  $1064^{\circ}$ . L. M. J.

**Heats of Dissolution of Solid and Liquid Ammonia, and the Latent Heat of Fusion of Solid Ammonia.** By GUSTAVE MASSOL (*Compt. rend.*, 1902, 134, 653—655).—From the determinations of the heats of dissolution of solid and of liquid ammonia at temperatures very near to  $-75^{\circ}$ , the melting point of the solid, the author calculates



the latent heat of fusion. The values obtained for the molecular heat of dissolution in 100 molecules of water were: Liquid, +1.77 Cal.; solid, -0.068 Cal., from which the value 1.838 Cal. results for the molecular latent heat of fusion, a number not far removed from that of water, 1.43 Cal.

L. M. J.

**Thermal Equivalent of Dissociation and Vaporisation, the Heat of Solidification of Ammonia.** By ROBERT DE FORCRAND (*Compt. rend.*, 1902, 134, 708—711).—In the case of a solid dissociable compound of a gas, such as the compounds of ammonia with various metallic chlorides, the relation holds  $Q_1/T_1 = Q_2/T_2 = k$  (about 30), hence  $(Q_1 - Q_2) = k(T_1 - T_2)$ . The value  $(T_1 - T_2)/(Q_1 - Q_2)$  is what the author terms the thermal equivalent of the dissociation, and in the case of the compounds mentioned, although the values of  $(T_1 - T_2)$  vary from 17.9° to 212.5°, yet the mean of the above quotient is about 31.1°. For gaseous ammonia,  $Q/T = k$ , where  $Q$  is the total heat of solidification  $L + S$ . By this means, the value for  $L + S$  can be calculated, the result obtained being 7.695 Cal.

L. M. J.

**Latent Heat of Solidification of Liquid Ammonia.** By ROBERT DE FORCRAND and GUSTAVE MASSOL (*Compt. rend.*, 1902, 134, 743—745).—The mean value for the heat of dissolution of liquid ammonia obtained by different methods is 1.882 Cal.; this, with Massol's determination of the heat of dissolution of solid ammonia, -0.068 Cal., leads to the value 1.95 Cal. for the molecular heat of fusion of ammonia, and from this the value  $7.695 - 1.950 = 5.74$  Cal. for the molecular latent heat of vaporisation is obtained. The difference between this and the value for water is in accord with the generalisation of de Forcrand (preceding abstract).

L. M. J.

**The Relation  $(L + S)/T = Q/T_1 = k$ .** By ROBERT DE FORCRAND (*Compt. rend.*, 1902, 134, 768—770).—From observations on ammoniacal metallic chlorides, the author has previously deduced the value 7.695 Cal. for  $L + S$  in the case of ammonia. The value of  $S$  has been directly determined and is 1.95 Cal. The value of  $L$  may be calculated by Clapeyron's rule from Regnault's determinations of the vapour pressure of ammonia. The values thus obtained fall regularly from 5.73 at 240.5° to 5.22 at 323° absolute, the first value being that at the boiling point under 760 mm. The value  $L + S$  is hence  $5.73 + 1.95$  Cal., that is, 7.68 Cal., which is in good accord with the calculated value (7.695), and hence confirms the validity of the rule (this vol., ii, 60).

L. M. J.

**Relation between the Latent Heat of Evaporation and the Vapour Density.** By W. A. KURBATOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 250—287).—The author describes a method for determining the latent heat of evaporation of compounds which readily solidify, a sketch of the apparatus used being also given. The total heat required to convert solid aniline hydrochloride into vapour is determined, and also the heat absorbed in melting the salt and heating it to the boiling point. These measurements having been made at various

pressures, the differences between the corresponding pairs of numbers give the latent heats of evaporation at the different pressures. The values of these latent heats are: Under 760 mm. pressure (b. p.  $244^{\circ}$ ), 252.0 Cal.; under 473 mm. (b. p.  $230^{\circ}$ ), 241.4 Cal.; under 394.6 mm. (b. p.  $225^{\circ}$ ), 252.7 Cal.; under 562 mm. (b. p.  $235^{\circ}$ ), 246.4 Cal.; under 442.1 mm. (b. p.  $227.9^{\circ}$ ), 242.6 Cal.

By means of the Clausius-Clapeyron formula, the amounts of dissociation at the boiling points under different pressures may be calculated, and in this way it is found that at its boiling point ( $244^{\circ}$ ) under 760 mm. pressure, aniline hydrochloride undergoes complete dissociation, whilst at a temperature  $15-20^{\circ}$  lower than this, about 10–15 per cent. of the salt remains undissociated in the state of vapour. There is no dissociation in the liquid salt.

The author shows that Trouton's law, namely,  $\rho M/T = \text{a constant}$  ( $\rho$  being the latent heat of evaporation,  $M$  the molecular weight, and  $T$  the absolute boiling point), can be derived from the Clausius-Clapeyron formula, and hence must not be regarded as a mere coincidence, but as a general law for all liquids. For a series of 98 organic and inorganic liquids for which data are available, the value of the above expression varies between 19.6 and 22.45, the mean number being about 21. Acetic, formic, butyric, and valeric acids, nitrogen peroxide, boron chloride, nitromethane, nitroethane, acetone, chloral hydrate, and chlorosulphonic acid are exceptions to this rule, as also are the following series of compounds: Water and the alcohols, which all give a constant somewhat greater (22.36–28.2) than 21; the nitriles, for which the constant is low, ( $-19.5-19.97$ ); and amylamine, which is the only amine for which the data are known, and which gives a value 23.3.

The relation brought forward by Linebarger, namely,  $\rho M/T' + 2 \log p = \text{a constant}$  (where  $\rho$  is the latent heat of evaporation,  $M$  the mol. weight,  $T'$  the absolute boiling point at the pressure  $p$ ) is not upheld by the experimental data, the value of the expression varying to the extent of 12–15 per cent. for a liquid boiling under different pressures.

T. H. P.

**Vapour Pressure in the System, Water-Acetone-Phenol. II.** By FRANZ A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1902, 40, 440–464. Compare this vol., ii, 243).—By plotting the results previously obtained at  $56.5^{\circ}$  on a system of coordinates, the composition of the mixtures which boil at this particular temperature and at a given pressure can be ascertained. For the pressure 300 mm., the results are graphically represented on a triangle. There are eight mixtures which boil under the given conditions ( $56.5^{\circ}$  and 300 mm.), and when the compositions of these are introduced into the diagram it is found that four of them lie on a straight line and are contained within the binodal curve. Any mixture the composition of which is represented on this line separates into two layers, the compositions of which are given by the points where the binodal curve cuts the line; they all boil at  $56.5^{\circ}$  under a pressure of 300 mm. The line made up of two curves and a straight part is the “vaporisation curve,” and a corresponding “condensation curve” is introduced into the diagram. These

curves divide the triangle into three fields: a gaseous, a liquid, and a heterogeneous. As the pressure decreases, the vaporisation curve is so displaced that the liquid field becomes smaller and ultimately coincides with the side of the triangle representing water and phenol. Increase of pressure increases the liquid field, so that at 760 mm. (temperature  $56.5^{\circ}$ ) all the components, all binary, and all ternary mixtures must be liquid. The composition of mixtures which boil at  $56.5^{\circ}$  under various pressures is also given in a table.

The composition of the phases of a three-phase system consisting of two liquids and a vapour in equilibrium is represented in a triangular form, and this may be used to ascertain the distillation pressure and the composition of distillate and residue.

The vaporisation curves at temperatures  $50^{\circ}$ ,  $68^{\circ}$ , and  $75^{\circ}$  are given for various pressures. At  $50^{\circ}$ , the vapour pressure of the critical liquid is 305 mm. Another critical liquid has the vapour pressure 550 mm. at this same temperature, but this is made up from the system water-phenol. At  $75^{\circ}$ , the binodal curve lies wholly within the triangle, and within the liquid field at a pressure of 760 mm., therefore all two-layer systems can be realised at the ordinary atmospheric pressure. The vapour pressure of the critical liquid at this temperature is 685 mm., that of the other critical liquid being 310 mm. As the temperature rises, these two points approach each other and coincide at  $92^{\circ}$ ; the composition of the critical liquid must therefore be regarded as a function of the temperature.

The author also describes how the results may be represented on a space model; provided that the temperature is kept constant, the vapour pressure can be represented as a function of two variables depending on the composition.

J. McC.

**Calorimetric Determination of the Form of Pressure Melting Point Curves.** By ARSENIA WYCHESLAVTZEFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, ii, 41—46).—The author has devised a modification of the method introduced by de Visser (*Abstr.*, 1893, ii, 563) for determining calorimetrically the value of  $\Delta v/\Delta r$ , the ratio of the change of volume to the corresponding heat of fusion. Multiplying this number by the mechanical equivalent of heat and by the absolute melting point of the substance gives  $dt/dp$ , which determines the form of the melting point curve. In de Visser's method, the calorimeter is immersed in a bath of the substance to be examined, a large quantity of which is hence required. The author therefore uses a bath of ordinary machine oil provided with a stirrer and thermostat; a sketch of the apparatus is given.

In the following table are given the values of  $dt/dp$  found in this way by the author, together with those determined by direct measurement by various investigators:

	Calorimetric.	Direct.
Naphthalene .....	0.0355	0.0351 and 0.0361
<i>o</i> -Nitrophenol .....	0.0202	0.0232 „ 0.0191
Phenol .....	0.0146	0.0144
<i>o</i> -Cresol .....	0.0156	—
Trimethylcarbinol .....	0.0262	—

T. H. P.

**Method of Determining the Freezing Point of a Solution at Constant Temperature.** By K. PRYTZ (*Ann. Physik*, 1902, [iv], 7, 882—892).—The freezing point of an aqueous solution can be defined as that temperature at which ice and a solution may be brought together without producing either a rise or fall of temperature, and on this definition the author's method is based. A Dewar vacuum vessel is filled with broken ice, and in it is suspended a Beckmann thermometer surrounded with a spiral tube ending near the bottom of the vessel. The solution the freezing point of which is to be determined is well cooled, and then allowed to flow slowly through the spiral tube and up through the broken ice round the thermometer. The thermometer gradually falls and ultimately remains constant at the freezing point of the solution; this point is independent, within certain limits, of the rate of flow of the solution and of the external temperature. The author claims that the above procedure has several advantages over the usual method.

It is estimated that when the outer wall of a vacuum vessel such as that used by the author (6 cm. internal diameter) is 1° higher in temperature than the interior, each square centimetre of the inner wall receives 0.00006 gram cal. per minute. J. C. P.

**Cryoscopic Researches.** By PAUL D. CHRUSTCHOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 153—182; 323—350. Compare Abstr., 1901, ii, 86 and 373).—The author has made use of the method previously described by him (*loc. cit.*), and here described in detail with the aid of sketches of the apparatus, to measure the depressions of freezing point of aqueous solutions of sodium and potassium chlorides, potassium bromide and sulphate, lead nitrate, sulphuric acid, and sucrose. From the results obtained, it is concluded that: (1) the method is sensitive and accurate; (2) the magnitude of the coefficient of depression (depression divided by concentration), and hence the mol. depression of freezing point, is not dependent on the dilution for all aqueous solutions. The way in which, in some cases, the mol. depression varies with the dilution is not in accord with the theory of dissociation as put forward by Arrhenius. T. H. P.

**Liquefaction of Gaseous Mixtures.** By F. CAUBET (*Zeit. physikal. Chem.*, 1902, 40, 257—367).—A brief history is first given of previous observations and discussions concerning critical phenomena, and a complete bibliography is added. The mixtures examined by the author were: (1) carbon dioxide and sulphur dioxide, (2) carbon dioxide and methyl chloride, (3) methyl chloride and sulphur dioxide. In the first system, eight separate mixtures were investigated, in which the concentration of the carbon dioxide varied from 0.10346 to 0.91095; the critical relations for the two pure gases are obtained from the observations of Cailletet and Mathias, and of Amagat. The relations between specific volume and temperature are first considered, the mixture containing 0.47103 of carbon dioxide being taken as an example. For this mixture at 46.2°, the specific volume of saturated vapour is 20.33 c.c., and of the liquid 1.318 c.c.; at 56.8°, the corresponding values are 14.101 and 1.499; at 70° they are 9.973 and 1.607. At 86°, the specific volume of the saturated vapour is

5.917, and when the volume decreases drops of liquid appear which increase until they possess the specific volume 2.223, when by a slight motion of the stirrer (an iron stirrer inside the tube and moved by an electro-magnet), the whole system becomes homogeneous. This is hence the critical temperature. At 88°, that is, above the critical temperature, liquid drops are formed when the specific volume reaches 5.4 c.c.; these increase until the quantity of liquid reaches a maximum, when they decrease and disappear at the specific volume 2.295. At 92.8°, drops of liquid appear, and disappear at the same specific volume, 3.7 c.c., so that this is the maximum temperature at which liquid can be formed, and between this and the critical temperature the system has no specific volume in the liquid state and two values of specific volume in the state of saturated vapour. Between these two temperatures, retrograde condensation is observed. The curves for all the mixtures are given, and from these the form of the critical line can be seen, although it is only clearly shown in a spatial projection in which a third axis of concentration is added. The curves representing pressure against temperature are next considered; at temperatures below the critical temperature, two important points are obtained—(1) the dew point, when liquid drops first form, and (2) the boiling point where the liquid phase alone exists. The values of these two points for the previous mixture are 56.8°, 29.6 and 69 atms.; 70.4°, 41 and 82.4 atms.; 83°, 57.2 and 92 atms. At 86°, the dew point is at 63.4 atms., and the critical point 93 atms. Above the critical temperature, no boiling point results, but two dew points with an intermediate pressure at which the liquid is a maximum. At 91.4°, these pressures are 76, 88, 92.2 atms. The critical line is hence the line at which the boiling point and dew point surfaces meet. The form of the isotherms is next considered; the course is that of a simple gas until the dew point is reached, when a discontinuity occurs, and the curve becomes less steep (ordinates = pressure); it, however, still slopes upward, in this respect differing from the isotherm of a single fluid, until the boiling point is reached, when the isotherm again becomes steeper. In the critical isotherm, however, there is no discontinuity at this second point, the isotherm being continuous from the two-phase to the one-phase system. Retrograde condensation is fully examined in those mixtures in which it is best observed, and tables of the volume of the liquid phase at different pressures between the two dew points are given for various temperatures. The author states that the appearance of the liquid is so different during retrograde condensation that it cannot be mistaken, the meniscus is flat, and the internal friction is far less than that of the liquid below the critical temperature, this being rendered very evident by the motion of the stirrer. At any given temperature and pressure, the composition of liquid and vapour in equilibrium is fixed, and as the dew point curve gives the values of the concentration of the vapour in equilibrium with liquid at various values of temperature and pressure, whilst the boiling point curve gives the composition of the liquid in equilibrium with vapour, the compositions of liquid and vapour in equilibrium with each other are readily obtained, and tables of these values are given. The specific volumes

are also calculated and shown by curves; at the critical temperature, the curves become continuous. The system methyl chloride and carbon dioxide was very similar, but in the case of the methyl chloride and sulphur dioxide system at certain concentrations the dew point and boiling point lines are tangential at certain points. These points are the points of Gibbs and Konowaloff. At such a point, therefore, there is no change of pressure during liquefaction, and the mixture at this temperature behaves like a single substance with a horizontal isotherm during the two-phase portion. In such a system, two equilibrium systems with double phase may occur at a given temperature and pressure; where this occurs, both phases in the one system must be more concentrated than the corresponding phases in the second. The paper concludes with a full account of the apparatus and experimental methods (Abstr., 1901, ii, 147, 148). L. M. J.

**Application of Optical Observations to the Study of Diffusion.** By J. THOVERT (*Compt. rend.*, 1902, 134, 594—596).—The paper contains the results of experiments obtained by the method previously described (this vol., ii, 197), and coefficients of diffusion are given for a number of salts and acids at various concentrations. The author states that the values for the salts are in good accord with those deduced according to Nernst's theory from electrolytic data, but in the case of acids the values are lower than those so calculated. L. M. J.

**Osmotic Properties of Colloidal Solutions.** By BENJAMIN MOORE and WILLIAM H. PARKER (*Amer. J. Physiol.*, 1902, 7, 261—293).—See this vol., ii, 413.

**Theory of the Velocity of Chemical Reactions.** By HANS EULER (*Zeit. physikal. Chem.*, 1902, 40, 498—503).—A reply to Wegscheider's objections (this vol., ii, 9) to the theory of ester hydrolysis already developed by the author (Abstr., 1901, ii, 532). If the constants,  $k$ ,  $\kappa$ , and  $K$  of the equations: (a)  $-d[\text{ester}]/dt = k[\text{ester}][\text{water}]$ ; (b)  $-d[\text{ester}]/dt = \kappa[\text{ester}][\text{HCl diss.}]$ ; and (c)  $-d[\text{ester}]/dt = [\text{ester}]\{[\text{water diss.}] + K[\text{HCl diss.}]\}$ , can be determined, the existence of an intermediary reaction must be assumed in order to explain the catalysis. J. McC.

**Decomposition of Mercurous Chloride by Dissolved Chlorides.** A Contribution to our Knowledge of Concentrated Solutions. By THEODORE W. RICHARDS and E. H. ARCHIBALD (*Zeit. physikal. Chem.*, 1902, 40, 385—398).—The action of concentrated solutions of sodium chloride on mercurous chloride and the disturbing effects caused by this in the Ostwald normal element were formerly noticed by Richards (Abstr., 1898, ii, 7), and it was suggested that the action might be a catalytic one. The amount of mercury salt found in solution when calomel is shaken with solutions of various concentrations of the chlorides of hydrogen, sodium, barium, and calcium, have been determined. The dissolved mercury exists wholly in the mercuric condition. The results are graphically represented, and from the curves it can be seen that as the concentration of the sodium chloride

increases, the quantity of dissolved mercuric chloride rises continuously; with hydrochloric acid, a maximum solubility is reached when the acid is about 7*N*, and at higher concentrations the amount dissolved remains practically constant. Calcium chloride also shows a maximum solvent power at about 7*N*. The action of the dissolved chloride is not catalytic, and the extent to which it proceeds is a simple function of the square of the concentration of the chlorine ions. The results can be satisfactorily explained by assuming that a complex ion  $\text{HgCl}_4^{2-}$  is produced which is highly dissociated (compare Le Blanc and Noyes, *Abstr.*, 1890, 388).

The system is one with four components, namely, water, dissolved salt, mercury (formed by reduction), and mercuric chloride, and when, at a definite temperature, the four phases—mercury, mercuric chloride, solution, and vapour—are present, there is only one degree of freedom required to define the system; this appears to be the concentration of the chlorine ions.

Similar reactions are effected by bromides and iodides, and, to a less extent, by sulphates.

Care must be taken, when precipitating mercury as mercurous chloride, to avoid the presence of much soluble chloride. J. McC.

**Decomposition of Organic Halogen Compounds by Sodium Amalgam in Alcoholic Solution.** By RICHARD LÖWENHERZ (*Zeit. physikal. Chem.*, 1902, 40, 399—439. Compare *Abstr.*, 1900, ii, 338; 1901, ii, 308).—The reaction between sodium amalgam and iodobenzene in alcoholic solution has been studied in detail; experiments have also been made using *isobutyl* iodide, *isobutyl* bromide, and bromobenzene. The reaction is not so simple as when sodium alone is used and the value of  $k = 1/(\text{Na}) \cdot \log. a/(a-x)$  is not by any means constant; (*Na*) is the quantity of dissolved sodium, *a* the original amount of halogen compound, and *x* the quantity decomposed. The quantity of water contained in the alcohol is without influence on the course of the reaction.

The results with iodobenzene show that the presence of dissolved sodium (as ethoxide) or of sodium iodide formed in the reaction has no effect on the value of *k*. The decomposition of iodobenzene by sodium amalgam is not directly proportional to the concentration of the iodobenzene; as the concentration of the iodobenzene decreases from 0.4 gram-mol. to 0.0015 gram-mol., the value of *k* rises from 0.67 to 30.3. The influence of temperature on the decomposition is so small that it cannot be determined. No influence can be traced to the surface area of the amalgam. Similar results have been obtained with potassium and lithium amalgams.

The decomposition of bromobenzene by sodium amalgam takes place extremely irregularly, so that the value of *k* varies with circumstances and even in parallel experiments the same value cannot be obtained; the influence of rapid stirring is particularly noticeable. The behaviour of *isobutyl* bromide is very similar to that of bromobenzene.

Chlorobenzene in alcoholic solution, when shaken with sodium amalgam, is only decomposed to the extent of about 1 per cent. One of the chlorine atoms of chloroform is easily removed by treatment

with sodium amalgam but further decomposition is exceedingly slow.

The author discusses the results of his investigation in connection with Kekulé's method of estimating halogen in organic compounds.

The difference in the reaction caused by sodium and that brought about by sodium amalgam is possibly due to secondary reactions taking place when amalgam is used. J. McC.

**The System Bismuth Oxide, Nitric Acid, and Water.** By G. M. RUTTEN (*Zeit. anorg. Chem.*, 1902, 30, 342—405).—Full details are given of work already described (Abstr., 1901, ii, 24). J. C. P.

**Method of Calculating Solubilities and the Equilibrium Constants of Chemical Reactions, and a Formula for the Latent Heats of Vaporisation.** By ALEXANDER FINDLAY (*Proc. Roy. Soc.*, 1902, 69, 471—478).—Ramsay and Young have shown (*Phil. Mag.*, 1886, [v], 21, 33) that if the complete vapour pressure curve of one substance and the vapour pressure of another substance at two temperatures are known, the vapour pressure curve of the second substance can be deduced from that of the first. The relation between the two vapour pressure curves may be expressed by the equation  $R = R' + c(t' - t)$ , and the author finds that a precisely similar equation connects the solubility curves of two substances; in this case,  $R$  and  $R'$  are the ratios of the absolute temperatures at which the substances have equal solubilities,  $c$  is a constant with a small positive or negative value,  $t'$  and  $t$  are the two temperatures at which the solubility of the second substance is known. The applicability of the equation has been tested with very satisfactory results on such pairs of substances as zinc chloride and bromide, potassium chloride and bromide, cadmium bromide and potassium nitrate, *m*- and *p*-hydroxybenzoic acids. The equation is independent of the state of ionisation of the dissolved substance, and of the sign of the heat of solution.

The temperature curves of the equilibrium constants of two reactions, even of quite different types, are related in a like manner, and an equation similar to the one quoted above is shown to apply satisfactorily to the reactions  $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$  (Bodenstein, Abstr., 1899, ii, 637) and  $2\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2 \rightleftharpoons \text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3)_2\cdot\text{OH}$  (Koelichen, Abstr., 1900, ii, 395).

The latent heat of vaporisation of a substance can be calculated, within a certain range, from the latent heat of vaporisation of another substance by means of the empirical equation  $L_1 = L_2 T_2^x$ , where  $L_1$  is the latent heat of the first substance at the absolute temperature  $T_1$ ,  $L_2$  the latent heat of the second substance at  $T_2$ , at which the vapour pressure of the second substance is equal to that of the first substance at  $T_1$ , and  $x$  is a constant. This relation holds very well in such cases as benzene and methyl acetate, or benzene and ethyl alcohol.

J. C. P.

**Catalysis of Hydroxylamine and Hydrazine.** By SIMEON TANATAR (*Zeit. physikal. Chem.*, 1902, 40, 475—480).—Berthelot's observation that hydroxylamine in alkaline solution decomposes according to the equation:  $3\text{NH}_3\text{O} = \text{NH}_3 + \text{N}_2 + 3\text{H}_2\text{O}$ , has been



confirmed. Another reaction, however, takes place simultaneously and the evolved gas contains about 5 per cent. of nitrous oxide. It may be assumed that this nitrous oxide is produced by oxidation of hydroxylamine by itself:  $4\text{NH}_2\text{OH} = 2\text{NH}_3 + \text{N}_2\text{O} + 3\text{H}_2\text{O}$ . When platinum black is used as catalyser, the decomposition takes place rapidly and the evolved gas contains much nitrous oxide and only 11 to 17 per cent. of nitrogen. In neutral solution, the decomposition is slow. This is a case of a reaction in which the products differ when direct decomposition takes place and when a catalyser is used.

The author explains the catalysis by the theory proposed by Engler and Wöhler (this vol., ii, 127) according to which the platinum acts as an oxygen-carrier. The hydroxylamine oxidises the platinum and this oxide then oxidises another part of the hydroxylamine. The platinum oxide formed does not separate iodine from potassium iodide, and it is soluble in hydrochloric acid.

Hydrazine sulphate in aqueous solution is quickly decomposed in presence of platinum black and this does not favour the view expressed on the mechanism of the reaction, for hydrazine cannot directly oxidise platinum; the oxidation of the platinum may, however, take place at the expense of the water present:  $3\text{N}_2\text{H}_4 + 3\text{H}_2\text{O} = 6\text{NH}_3 + 3\text{O}$ ;  $3\text{N}_2\text{H}_4 + 3\text{O} = 3\text{H}_2\text{O} + 2\text{NH}_3 + 2\text{N}_2$ . Possibly the two catalyses are different.  
J. McC.

**Inhibition of Chemical Reactions by Foreign Substances. I.**  
By STEWART W. YOUNG (*J. Amer. Chem. Soc.*, 1902, **24**, 297—327).—It has been shown (Abstr., 1901, ii, 391) that the rate of oxidation of solutions of stannous chloride by means of oxygen is greatly diminished by the presence of small quantities of poisonous substances, especially alkaloids.

The rate of action of nitrous oxide and of nitric oxide on sodium sulphite is not appreciably affected by the presence of brucine, and it appears therefore that the inhibitory action is confined to reactions in which free oxygen is involved.

The effect of a number of substances on the rate of oxidation of sodium sulphite by oxygen has been investigated with the following results. The presence of brucine hydrochloride in a neutral solution causes a considerable retardation, but in alkaline solution its effect is much greater; in the latter case, the rate of oxidation is reduced to less than 0.01 of the normal rate by the presence of the brucine salt of a concentration 1/200,000 molar. In acid solutions, the influence of brucine is much less than in neutral solutions, and the period of development of the inhibitive action is longer. The effect of quinine hydrogen sulphate in neutral solution is considerably less than that of brucine hydrochloride, but in alkaline solution a concentration of 1/2600 molar is sufficient practically to stop the oxidation of the sodium sulphite. Morphine hydrochloride, atropine sulphate, sucrose, glycerol, potassium cyanide, ammonium chloride, sodium acetate, pyrogallol, *p*-hydroxybenzoic acid, hydroxylamine hydrochloride, and ethyl alcohol also have the power of inhibiting the oxidation of sodium sulphite, and in each case the effect produced is much greater in alkaline than in neutral solution. Determinations were made of the

velocity of oxidation in presence of each of these substances, and the results are tabulated.

A series of experiments was carried out with the object of determining the minimum concentration of certain substances necessary to produce a measurable inhibiting effect. The limit of dilution differs for different substances, the effect in some cases being still appreciable at a dilution of  $1/2,600,000$  molar.

The inhibitive effect has been shown in every case to be not instantaneous, but to develop slowly with the oxidation of the solution. In many cases, it was found that after the addition of the inhibiting agent an initial acceleration occurred.

E. G.

**Molecular Weight of Liquid Water, and Ostwald's Dilution Law.** By WILHELM VAUBEL (*Zeit. angew. Chem.*, 1902, 15, 395—398).—The author rehearses the grounds for his view that the molecule of liquid water is  $(H_2O)_6$ , and that electrolytic dissociation is conditioned by a combination of anion or cation with the molecular complex  $(H_2O)_5$ , or  $(H_2O)_6$ . Combining this hypothesis with the law of mass action, he deduces the form of the dilution law arrived at empirically by van't Hoff.

J. C. P.

**Molecular Weights of some Carbon Compounds in Concentrated Solutions with Carbon Compounds as Solvents.** By CLARENCE L. SPEYERS (*Amer. J. Sci.*, 1902, [iv], 13, 213—223. Compare Abstr., 1898, ii, 213; 1899, ii, 145; 1900, ii, 10).—By a slight modification of Walker's method (Abstr., 1899, ii, 6), the author has determined the molecular weights of non-volatile organic substances such as carbamide, resorcinol, acetanilide, naphthalene, acenaphthene, and benzamide in one or more of the following solvents: water, methyl, ethyl and propyl alcohols, and toluene; the solutions contained in some cases as much as 60 per cent. of dissolved substance. The molecular weight has been calculated by both the formulæ  $n/N = (p - p')/p'$  and  $n/N = l(p/p')$ , but the values obtained point rather to the superiority of the former.

The author deduces the equation  $l(n/N + 1) = Q'/R \cdot (T_1 - T_0)/T_1 T_0$ , where  $Q'$  is the heat of vaporisation of 1 gram-mol. of solvent from the solution (the quantity of solution being very large),  $R$  is the gas constant,  $T_1$  and  $T_0$  the boiling points of the solution and solvent respectively. This equation is independent of the osmotic theory and may be used to determine molecular weights according to the boiling point method, or to determine the heat of vaporisation of the solvent.

J. C. P.

**Researches on Physical Changes in the Condition of Colloids. I. Behaviour of Gelatin.** By WOLFGANG PAULI and PETER RONA (*Beitr. chem. Physiol. Path.*, 1902, 2, 1—41. Compare Pauli, Abstr., 1900, i, 265).—The influence of crystalloids on the behaviour of colloids is traced in the changes produced in the points of fusion and solidification of gelatin by the addition of various organic and inorganic substances. Ammonium sulphate and sodium acetate raise the points of fusion and solidification, whilst sodium and

ammonium chlorides have the opposite effect; variation of the percentage of gelatin leaves the relative influence of these salts unaltered, and for all concentrations of gelatin the influence of the cation is insignificant compared with that of the anion. The curve connecting the melting point of gelatin with the concentration of the latter is concave to the concentration axis, and this is the case also in the presence of any of the above-mentioned salts. The corresponding curves for the solidification point are practically straight lines, and from this difference in behaviour the authors conclude that gelatin about to melt is in a different condition from gelatin about to solidify, the temperature and concentration being the same.

The united effect of two crystalloids (in equivalent concentration) on the solidification and fusion of 10 per cent. gelatin is the algebraic sum of the individual effects. This result has been established with combinations of precipitating and non-precipitating salts, of electrolytes and non-electrolytes, and of non-electrolytes among themselves. The alteration of dissociation produced when two salts with a common ion are taken has apparently no effect on the solidification of gelatin.

The influence of crystalloids on the precipitation of gelatin from its solutions is entirely distinct from the influence exerted by them on the solidification and fusion points. Thus precipitation is effected only by electrolytes, whilst both electrolytes and non-electrolytes may help or hinder solidification. Again, salts which are alike in precipitating gelatin may have opposite effects on the solidification and fusion points. It has further been observed that dissociation of the salts is an important factor in the precipitation of gelatin. The precipitating power of salts is diminished by the addition of non-electrolytes, such as sucrose, dextrose, and especially carbamide. The author argues against Hardy's view that in the process of solidification of a gelatin solution two phases are formed, although this is doubtless the case in the precipitation of gelatin by electrolytes.

J. C. P.

**Report of the [American] Committee on Atomic Weights.** By FRANK W. CLARKE (*J. Amer. Chem. Soc.*, 1902, 24, 201—215).—A résumé of the work published during 1901 on the atomic weights of nitrogen, calcium, arsenic, antimony, tellurium, tungsten, uranium, lanthanum, praseodymium, neodymium, thorium, indium, yttrium, ytterbium, &c.; a corrected table of the atomic weights of all the elements is appended.

E. G.

**The Theory of Partial Valencies.** By EMIL ERLLENMEYER, junr. (*J. pr. Chem.*, 1902, [ii], 65, 346—364).—A reply to Thiele (this vol., i, 151) and in part to Graebe (this vol., i, 209).

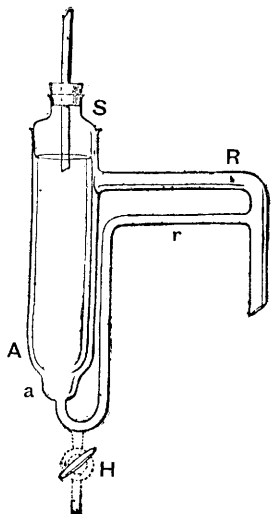
G. Y.

**Modified Forms of an Adapter for Vacuum Distillation and of a Thermo-Regulator.** By THOMAS S. PATTERSON (*J. Soc. Chem. Ind.*, 1902, 21, 456—457).—The adapter consists of a bulb-shaped flask, about 55 mm. in diameter. The neck is closed by a cork through which passes a narrow glass tube connecting the apparatus to the condenser. The portion of this tube inside the flask is bent towards the lower sides of the latter so that it will deliver the distillate into

one or other of three or more glass tubes sealed into the lower part of the flask, so that, by rotating the apparatus, the distillate may run into separate flasks connected to the tubes. A central tube at the bottom of the flask is placed in connection with the pump.

In the thermo-regulator described, the end of the mercury tube is closed by a cap of thin sheet india-rubber. Against this is placed the end of the gas supply tube, the latter being cut off at a very slight angle. The bulging of the india-rubber cap cuts off the supply of gas. The working temperature of the apparatus is set by means of a side tube on the mercury column, provided with a tap and small funnel through which mercury may be added or allowed to escape. The lower end of the mercury column is bent upwards and widens out into a bulb which may be filled with toluene or, possibly, air. W. P. S.

**Universal Extraction Apparatus for Solvents with High and Low Boiling Points.** By ANTON LANDSIEDL (*Chem. Zeit.*, 1902, 26, 274—275).—The apparatus consists of the extractor, *A*, the tube, *R*, which admits the vapour of the solvent and is connected with a distilling flask, and the tube, *r*, through which the extract runs back into the flask. The apparatus is attached to a reflux condenser by



means of the perforated cork, *S*. It may be used for the extraction of solids, or of liquids which are lighter than the solvent. Powders are either enclosed in a filter paper cartridge, or put as such into the extractor after having introduced at *a* a plug of glass or cotton-wool and also some solvent. The substance should on no account reach higher than the level of the horizontal part of the tube *r*. When a liquid has to be extracted, *a* is filled with solvent and the sample is poured on to the surface. The condensed solvent penetrates the liquid, collects at the bottom, and then runs back through *r* into the flask. The stopcock, *H*, serves for the purpose of collecting some of the solvent to see whether the extraction is complete, of allowing the solvent in the flask to be removed by distillation, and also of rapidly emptying the extractor. Two modifications of the apparatus are described in the paper.

In one of them (for solids only) the stopcock is absent, and the solvent, instead of continually flowing back into the flask, collects, and is then automatically removed by a syphon. The other serves for the extraction of liquids which are heavier than the solvent used.

L. DE K.

**Condensers and Reflux Condensers.** By ANTON LANDSIEDL (*Chem. Zeit.*, 1902, 26, 325—326).—The apparatus may be used for ordinary as well as fractional distillation and also serves as a reflux apparatus. It consists of the condenser, *A*, at the bottom of which is

sealed a wide and strong tube, *E*, which admits the vapours, of the worm, *B*, which further cools the condensed liquid, which then runs through *C* into a receiver, and of a jacket with a water inlet at *a* and outlet at *c*. During fractional distillations, the ground stopper from *E* is removed, and a thermometer inserted. When the apparatus is used as a reflux condenser, it is only necessary to close the stopcock near *B*; all but a few c.c. of the distillate runs back through *E* into the distilling flask.

A modification of the apparatus is also described.

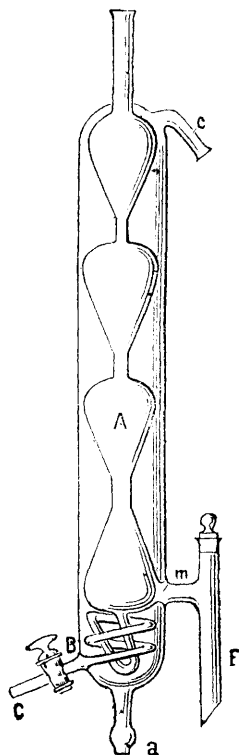
L. DE K.

**New Apparatus.** By CHARLES B. WILLIAMS (*J. Amer. Chem. Soc.*, 1902, **24**, 246—248).—The author has devised (1) an instrument for marking volumetric flasks. (2) A bulb delivery tube for use in distilling ammonia in nitrogen estimations. The latter consists of an ordinary bulb delivery tube, the lower end of which is closed with the exception of a 2 mm. hole; 6 or 7 mm. above this end are four perforations arranged at equal distances round the tube, the object being to distribute the ammonia, and thus increase the facility for absorption by the acid. For details, the description and diagrams in the original must be consulted.

E. G.

**Some Lecture Experiments.** By F. BODROUX (*Bull. Soc. Chim.*, 1902, [iii], **27**, 349—351).—The author describes several experiments to illustrate combination between solid substances. When water is dropped on a mixture of magnesium filings or zinc dust and iodine, violent reaction occurs, but the experiment is much more brilliant if a mixture of aluminium powder and iodine be employed. In this case, the mass inflames and the combustion propagates itself throughout the mass.

A. F.



### Inorganic Chemistry.

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The Question of Hydrogen in the Atmosphere. By LORD RAYLEIGH (*Phil. Mag.*, 1902, [vi], 3, 416—422. Compare Gautier, *Abstr.*, 1900, ii, 538; Rayleigh, *Abstr.*, 1901, ii, 141).—From the

author's experiments it follows that the free hydrogen in country air does not exceed one part in 30,000 by volume. The method employed was to pass 10 litres of the dried air over heated copper oxide and absorb the water formed in a phosphoric oxide tube. J. C. P.

**Composition of Chlorine Hydrate.** By ROBERT DE FORCRAND (*Compt. rend.*, 1902, 134, 991—993).—From the heat of formation from ice and the heat of formation from liquid water, it is deduced that the formula of chlorine hydrate is  $\text{Cl}_2 \cdot 7\text{H}_2\text{O}$  (compare *Compt. rend.*, 1902, 134, 835). J. McC.

**Metallic Chlorates. Studies on the Solubility of Salts. X.** By ADOLPH MEUSSER (*Ber.*, 1902, 35, 1414—1424).—Measurements are given of the solubility of the chlorates of magnesium, zinc, cobalt, nickel, copper, and cadmium in water at different temperatures, as well as data with regard to the transformation points of their various hydrates. The following is a summary of the results. Hexa- and tetra-hydrates of the chlorates of zinc, magnesium, cobalt, and nickel can be obtained, and dihydrates of magnesium, zinc, cobalt, and nickel; in the case of cadmium chlorate, only the dihydrate is stable, and with copper chlorate only the tetrahydrate. In the case of the chlorates, 2 mols. of water are lost at a time, whilst with the analogous nitrates 3 mols. are lost; the solubility of the chlorates is much greater throughout than that of the nitrates. There appears to be no relationship between the order of solubility of the hexahydrates of the chlorates and nitrates of the same metals, but the order of solubility of the chlorates at low temperatures ( $-30^\circ$  to  $-20^\circ$ ) is that of the tension of their normal solutions. W. A. D.

**Behaviour of Hydrogen and Oxygen in Presence of Water.** By ARTURO MARCACCI (*Atti R. Accad. Lincei*, 1902, [v], 11, i, 324—326).—The author describes experiments which indicate that when hydrogen is left in a bell-jar over water, the gas is absorbed by the water and combines with the dissolved oxygen also present in the water. Confirmatory experiments are being made. T. H. P.

**New Method of Preparing Oxygen.** By GEORGE F. JAUBERT (*Compt. rend.*, 1902, 134, 778—779).—Pure oxygen is readily obtained by the action of water in a Kipp's or similar apparatus on compressed sodium peroxide, mixed before compression with the calculated quantity of a soluble permanganate or hypochlorite, or with traces of a nickel or cobalt salt. The peroxide,  $\text{KNaO}_3$ , obtained by the action of air on the liquid alloy of sodium and potassium, may be employed for the same purpose. C. H. B.

**Atomic Weight of Selenium.** By JULIUS MEYER (*Ber.*, 1902, 35, 1591—1593).—The percentage of silver in carefully purified silver selenite was determined by electrodeposition. The mean of five determinations by this method gave 79.21 as the atomic weight of selenium (compare Lenher, *Abstr.*, 1899, ii, 18). W. A. D.

**Compounds of Phosphorus and Selenium.** By JULIUS MEYER (*Zeit. anorg. Chem.*, 1902, 30, 258—264).—When selenium is dissolved in molten phosphorus, no compound is formed, but from the depression of the freezing point it is concluded that  $P_4Se$  and  $P_2Se$ , described by Hahn (*J. pr. Chem.*, 1864, 93, 430), do not exist. A mixture corresponding with the composition represented by  $P_4Se$ , when distilled in a current of carbon dioxide, gives pure phosphorus as distillate and selenium as residue. On heating a mixture of phosphorus and selenium in the mol. proportions 2 : 1, some phosphorus distils, then, at a higher temperature ( $360-400^\circ$ ), heavy, red vapours are formed which condense to oily drops, and these ultimately solidify. Analysis shows that this red substance has the composition  $P_4Se_3$ . It closely resembles  $P_4S_3$  in behaviour, and is very readily attacked by moisture.

Phosphorus, sulphur, and selenium, when fused in the proper proportions, give the compounds  $P_4S_3$ ,  $P_4S_2Se$ ,  $P_4SSe_2$ , and  $P_4Se_3$ . The melting point rises with the proportion of selenium, as the following values show :  $P_4S_3$ ,  $150-160^\circ$  ;  $P_4S_2Se$ ,  $190-200^\circ$  ;  $P_4SSe_2$ ,  $225-230^\circ$ , and  $P_4Se_3$ ,  $300^\circ$ .

On fusing a mixture of phosphorus and selenium in the mol. proportions 2 : 3, a substance is obtained which may be the compound  $P_2Se_3$  ; on distillation, it yields, first  $P_4Se_3$ , and at a red heat a dark substance passes over which, according to analysis, is  $P_2Se_5$ .

J. McC.

**Arsenic Oxide and its Hydrates.** By VICTOR AUGER (*Compt. rend.*, 1902, 134, 1059—1061).—A solution of arsenic acid, when heated at  $63^\circ$  for three days, gives a deposit of the hydrate  $H_6As_4O_{13}$ , which may be heated at  $165^\circ$  without altering, but at  $175^\circ$  loses water and is converted into the oxide. Fused arsenic oxide cannot be obtained pure, for below its melting point it gives off oxygen and leaves a residue containing arsenious oxide. The author concludes that the only hydrates known are  $H_8As_2O_9$  and  $H_6As_4O_{13}$ .

J. McC.

**Direct Combination of Chlorine and Carbon.** By WERNER VON BOLTON (*Zeit. Elektrochem.*, 1902, 8, 165—170).—When an electric arc is formed between carbon points in an atmosphere of carbon tetrachloride, the substance is rapidly decomposed into its elements. If, however, the arc is maintained in a small vessel (300 c.c.) in an atmosphere of chlorine which is not renewed, crystals are gradually deposited in the cooler parts of the vessel. These consist apparently of hexachlorobenzene. The yield is very small (0.02 gram in 6 hours with 42 volts and 5.5 amperes). With a larger vessel (2 litres capacity) divided into two parts by a constriction, large quantities of perchloroethane were formed. The arc was maintained in the upper chamber, and the lower one kept cold by means of a freezing mixture.

Similar results were obtained with bromine and iodine. They were not, however, followed up.

T. E.

**Classification and Atomic Weights of Neon, Argon, Krypton, and Xenon.** By HENRY WILDE (*Compt. rend.*, 1902, 134, 770—772).—



The author regards neon, argon, krypton, and xenon as belonging to the group of elements which includes nitrogen. In this group the atomic weight is represented by  $H \times 7n$ , and he takes the atomic weights to be respectively, 7, 21, 42, and 63. He assumes that the observed density of neon, 9.96, is too high in consequence of the difficulty of purifying it.

C. H. B.

**Decomposition of Sodium Nitrate by Sulphuric Acid.** By C. W. VOLNEY (*J. Amer. Chem. Soc.*, 1902, 24, 222—226).—It has been shown previously (Abstr., 1901, ii, 600) that the decomposition of sodium nitrate by concentrated sulphuric acid takes place in two distinct phases. Further experiments have led to the following conclusions. At temperatures below  $20^\circ$ , neither strong sulphuric acid nor the compound  $\text{NaH}_3(\text{SO}_4)_2$  reacts with sodium nitrate; at a higher temperature, decomposition occurs, and the first phase is completed below  $100^\circ$ . The second phase, in which the compound  $\text{NaH}_3(\text{SO}_4)_2$  reacts with the sodium nitrate, takes place at temperatures above  $165^\circ$ .

E. G.

**Redetermination of the Atomic Weight of Calcium.** By THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1902, 24, 374—377).—Two specimens of marble, one Italian, the other from Rutland, Vermont, U.S.A., were converted into calcium nitrate, which was carefully purified by recrystallisation. The nitrate was converted into the carbonate by precipitation with ammonium carbonate. The chloride was prepared from the carbonate, and was repeatedly recrystallised, ignited in a stream of hydrogen chloride and again recrystallised. Five analyses of three samples of calcium chloride, thus prepared, gave a mean value of 40.126 for the atomic weight of calcium ( $O=16$ ,  $\text{Cl}=35.455$ ) which agrees closely with that obtained by Hinrichsen (Abstr., this vol, ii, 137).

E. G.

**Action of Hydrogen on Strontium Amalgam.** By ANTOINE GUNTZ (*Compt. rend.*, 1902, 134, 838—840. Compare this vol., ii, 138, 208).—The dissociation pressure of strontium hydride at  $1000^\circ$  is 100 mm., and at  $1100^\circ$ , 300 mm.; from these values, by the aid of Clapeyron's formula, the heat of formation of strontium hydride from its elements is found to be +38.4 Cal. The heat of formation has also been indirectly determined by observing the heat change when strontium hydride is decomposed by water into strontium hydroxide and hydrogen; it amounted to +54.75 Cal.; as the heat of formation of strontium hydroxide is +158.7 Cal., the heat of formation of strontium hydride is +34.7 Cal.

On heating strontium hydride at  $1300^\circ$  in a current of hydrogen, strontium is obtained as a white, crystalline metal.

K. J. P. O.

**Solubility of Barium Sulphate in Ferric Chloride, Aluminium Chloride, and Magnesium Chloride.** By GEORGE S. FRAPS (*Amer. Chem. J.*, 1902, 27, 288—291).—The method employed was that of Fresenius and Hintz (Abstr., 1896, ii, 499), with the exception that

barium chloride was used in place of hydroxide. The following table shows the results obtained :

Concentration of "solvent" salt per litre, grams.	Milligrams (per litre) of BaSO <sub>4</sub> dissolved by		
	FeCl <sub>3</sub> .	Al <sub>2</sub> Cl <sub>6</sub> .	MgCl <sub>2</sub> .
1	58	33	30
2.5	72	43	30
5	115	60	33
10	123	94	33
25	150	116	50
50	160	170	50
100	170	175	50

The author also observed that, in presence of excess of barium chloride, barium sulphate is slightly less soluble in solutions of ferric and aluminium chlorides than in solutions of ammonium and sodium chlorides (2.5 per cent.) or in nitric and hydrochloric acids (2.5 per cent.).

T. A. H.

**Arsenides of the Metals of the Alkaline Earths.** By PAUL LEBEAU (*Ann. Chim. Phys.*, 1902, [vii], **25**, 470—483).—An account of work already published (compare Abstr., 1899, ii, 288, 655).

G. T. M.

**Nature of Alkaline Solutions of Metallic Hydroxides.** By ARTHUR HANTZSCH (*Zeit. anorg. Chem.*, 1902, **30**, 289—324).—By a study of (1) the conductivity of alkaline solutions of metallic hydroxides, (2) the rate at which these solutions saponify ethyl acetate, it is possible to estimate the extent of saponification of the salts formed by the combination of alkali and metallic hydroxide, and thence to deduce the relative strength of those hydroxides which appear to act as acids. The results, which are not quantitative in the strictest sense, have been arrived at by comparing the alkaline solutions of the hydroxides with solutions containing no hydroxide, but otherwise the same. The hydroxides of zinc, beryllium, lead, tin, and germanium all act as acids, the order given being the order of increasing strength. Of these, zinc and beryllium hydroxides are extremely weak acids; indeed, zinc hydroxide in alkaline solution appears to exist mostly in the colloidal form. Lead, tin, and germanium hydroxides have markedly acid properties, the last-mentioned being a weak electrolyte. All five hydroxides act as monobasic acids, and there is no ground for assuming the existence of such ions as ZnO<sub>2</sub>". It is noted that the order of the hydroxides given above is not exactly the reverse of the order in which they would be arranged according to their strength as bases. Thus lead hydroxide as a base is stronger than beryllium hydroxide, and it might be expected that as an acid it would be weaker; this, however, is not the case. The key to the exceptionally marked acid character of the hydroxides of lead, tin, and germanium is found in the ability of these metals to act as quadrivalent elements; so that

the plumbites, for example, are salts of the acid,  $\text{Pb} \begin{array}{c} \text{H} \\ \diagup \text{O} \\ \diagdown \text{OH} \end{array}$ , rather than

of the acid,  $\text{Pb} \begin{array}{c} \text{OH} \\ \diagup \text{O} \\ \diagdown \text{OH} \end{array}$ , this internal constitutional change being accompanied by a strengthening of the acid character. From this point of view, the hydroxides of lead, tin, and germanium are acids of the  $\text{H} \cdot \text{CO}_2\text{H}$  type, their relative acid character corresponding with the position of these elements in the periodic system. J. C. P.

**Solubility of Hydroxides of the Heavy Metals in Sodium Hydroxide.** By JACOB RUBENBAUER (*Zeit. anorg. Chem.*, 1902, 30, 331—337).—The quantities of beryllium, zinc, tin, and lead hydroxides dissolved by sodium hydroxide solutions vary with the concentration of the latter; this influence of concentration is very marked in the case of zinc, slight in the case of lead, and still less in the case of beryllium and tin. For zinc and lead hydroxides, there is a maximum value of the solubility when the atomic ratios are  $\text{Zn} : \text{Na} = 1 : 3$  and  $\text{Pb} : \text{Na} = 1 : 14$  respectively; for tin there is a minimum at the ratio  $\text{Sn} : \text{Na} = 1 : 7.7$ ; for beryllium neither maximum nor minimum has been found, the solubility of the hydroxide slowly increasing with increasing concentration of the sodium hydroxide solution. The existence of a maximum or minimum may be attributed to two independent factors:—(1) hydrolysis of the zincates, &c., formed, the hydrolysis increasing as the solutions become more dilute, and leading to a diminished solubility; (2) dehydration of the hydroxides by strong alkali, and transformation into a less soluble form, this factor tending to a diminished solubility with increasing alkali concentration; thus undissolved stannous hydroxide, on treatment with cold concentrated alkali, is converted into anhydrous stannous oxide.

When zinc hydroxide is treated with alkali, more dissolves at first than corresponds with the true equilibrium under the prevailing conditions, for such solutions spontaneously deposit more or less zinc hydroxide according to the concentration: the same appears to hold for beryllium hydroxide, but not for tin and lead hydroxides (compare Herz, this vol., ii, 77; Kuriloff, this vol., ii, 139).

J. C. P.

**Interpretation of Certain Modifications of Metallic Hydroxides.** By ARTHUR HANTZSCH (*Zeit. anorg. Chem.*, 1902, 30, 338—341).—Zinc hydroxide separates from its alkaline solution (see Rubenbauer, preceding abstract) in the form of a fine, dense powder, soluble only with difficulty in sodium hydroxide. In referring to this and other cases involving similar changes of properties (compare Herz, Abstr., 1900, ii, 728; 1901, ii, 513; this vol., ii, 82), the author argues against the assumption of isomerism or polymerism, and attributes the phenomena in question (1) to physical alteration of the surface (see Ostwald, Abstr., 1900, ii, 712); (2) to a dehydration of the hydroxides caused by alkalis; an organic parallel of the latter process is found in the formation of an anhydride of quinonedioxime (Farmer and Hantzsch, Abstr., 1900, i, 103).

J. C. P.

**Alloys of Cadmium with Calcium and Barium.** By HENRI GAUTIER (*Compt. rend.*, 1902, **134**, 1054—1056).—The alloys were prepared by heating a mixture of 175 grams of calcium iodide or 225 grams of barium iodide with 100 grams of cadmium and 50 grams of sodium to a red heat for two hours. The alloys so obtained contained 16 to 18 per cent. of alkaline earth metal; by distillation under reduced pressure, the percentage can be raised to about 45. The alloys rich in alkaline earth metal are decomposed by water; liquid bromine has no action on them, but they are attacked by bromine vapour or chlorine. Below a red heat, iodine has no action. They burn in oxygen or air. The action of sulphur is violent and sulphides are formed. Hydrogen and nitrogen give calcium or barium hydride or nitride under conditions which will be described later. J. McC.

**Analysis of an Antique Vase from Abou-Roach.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1902, [vii], **25**, 467—470).—Analyses of a vase found in the mortuary chapel of the pyramid of King Didoufri, who lived at the commencement of the fourth dynasty, show that this article was originally produced by baking together a mixture of fine sand, litharge, and sodium chloride. The chief constituents of the material composing the vase are silica, lead, chloride, and oxide, together with smaller amounts of calcium carbonate, calcium and sodium oxides, and water. G. T. M.

**Radioactive Substances. Radioactive Lead.** By KARL A. HOFMANN and V. WÖLFL (*Ber.*, 1902, **35**, 1453—1457. Compare this vol., ii, 261).—It is found that the radioactive material in lead can be most easily concentrated by dissolving the lead chloride in aqueous sodium thiosulphate; on being kept for some days, an extremely active black sulphide separates. It was compared with specimens of radium and polonium. Unlike polonium, radioactive lead acts on a photographic plate with great rapidity through an interposed sheet of gutta-percha. K. J. P. O.

**Thallous Sulphates.** By WILLEM STORTENBEKER (*Rec. Trav. Chim.*, 1902, **21**, 87—94).—Thallous sulphate crystallises especially well in rhombic prisms from a solution containing a small quantity of free sulphuric acid; excess of the acid prevents crystallisation. The salt is far more soluble in dilute sulphuric acid than in water.

On concentrating a saturated solution of the normal sulphate, which contains for each mol. of sulphate 10 mols. of sulphuric acid, the *acid sulphate*,  $\text{Ti}_2\text{SO}_4\cdot\text{TiHSO}_4$ , first separates in hexagonal leaflets; on further evaporation, *thallium hydrogen sulphate*,  $\text{TiHSO}_4$ , separates in four-sided, lustrous, monoclinic, hygroscopic plates melting at 115—120°, and also in rhombic needles.

The author finds that the method of estimating thallium as the hydrogen sulphate, recommended by Browning (*Abstr.*, 1900, ii, 247) is not satisfactory. It is better to estimate thallium as normal sulphate. K. J. P. O.

**Thallic Cæsium Sulphates.** By JAMES LOCKE (*Amer. Chem. J.*, 1902, **27**, 280—284).—When solutions of thallic and

cæsium sulphates are mixed in the quantities necessary for the formation of a cæsium-thallium alum, there separates at first the hydrated double sulphate,  $\text{CsTl}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ , which crystallises in colourless prisms of the rhombic system. The mother liquor, on concentration, deposits colourless, transparent plates of a second hydrated double sulphate,  $\text{CsTl}(\text{SO}_4)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ . The author has also attempted to prepare alums containing chromic in place of sulphuric acid by crystallising together aluminium chromate and cæsium dichromate, but no evidence of the formation of such salts was obtained. When sulphuric acid is added to the crystallising solution, cæsium aluminium alum separates.

T. A. H.

**Egyptian Metallic Tools.** By ALBERT COLSON (*Compt. rend.*, 1902, 134, 989—991).—The author describes a cold chisel dating from the Thébaines dynasty. It consists of two parts cemented together. The core contains 13·3 per cent. of tin and 84·6 per cent. of copper, and the envelope 4·7 per cent. of tin and 92·6 per cent. of copper.

J. McC.

**Cerium Peroxide.** By E. BAUR (*Zeit. anorg. Chem.*, 1902, 30, 251—257).—Cerosus sulphate solution containing potassium carbonate, when shaken with air, is converted into cerium peroxide, and at the same time some ceric salt is formed. A slight alkalinity of the solution increases the yield of peroxide. When arsenious oxide is used as "acceptor," the cerium is converted to a greater extent into peroxide.

By the method employed by Manchot and Wilhelms (*Abstr.*, 1901, ii, 658), the influence of cerium on the reaction between potassium iodide and hydrogen peroxide has been investigated. In neutral solution, cerous salts cause a separation of iodine, amounting to about two-thirds of an equivalent per equivalent of cerium; the action is, however, complicated by the fact that the ceric hydroxide formed has a catalytic influence which increases the amount of iodine separated, and, on the other hand, this is decreased, because the peroxide acts directly on the cerous oxide. The results are in agreement with the assumption that an intermediate product is formed, but they do not prove this.

The salt,  $\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot \text{O}_3 \cdot 4\text{K}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , described by Job (*Abstr.*, 1899, ii, 486), gives oxygen as well as carbon dioxide when treated with dilute sulphuric acid. More oxygen is liberated than indicated by the equation  $2\text{CeO}_3 + 3\text{H}_2\text{SO}_4 = \text{Ce}_2(\text{SO}_4)_3 + \text{O}_2 + \text{H}_2\text{O}_2 + 2\text{H}_2\text{O}$ , and this is due to a spontaneous decomposition of the hydrogen peroxide present.

J. McC.

**Solubility of Zinc Hydroxide in Ammonia and Ammonium Bases.** By W. HERZ (*Zeit. anorg. Chem.*, 1902, 30, 280—281).—The solubility of precipitated zinc hydroxide, dried at 60—70°, in solutions of ammonia and amines of various concentrations has been determined at the ordinary temperature (17—19°). It is insoluble in dimethylamine and diethylamine. From the results with ammonia, methylamine, and ethylamine, it is found that the more dilute the solution of the base the more molecules are required to dissolve the hydroxide. Substitution of a hydrogen atom of ammonia by an

alkyl group decreases the solubility, the depression increasing with the mol. weight of the substituting group. J. McC.

**Cerium Oxycarbide.** By JEAN STERBA (*Compt. rend.*, 1902, 134, 1056—1059).—Cerium oxide, when heated in the electric furnace for one minute with a quantity of carbon (soot) insufficient for complete reduction and the product washed with ice water, gives a brown residue of the compound  $\text{CeC}_2, 2\text{CeO}_2$ . The sp. gr. at  $17^\circ$  is 4.8. It is stable in the air, and is only slowly attacked by cold water. With hot water or acids, it gives unsaturated hydrocarbons. It burns in the air with incandescence. It is acted on by fluorine at  $150^\circ$ , by chlorine, bromine, and iodine at a dull red heat, by hydrochloric, hydrobromic, and hydriodic acids at a red heat, and by sulphur at  $450^\circ$ . When fused in the electric furnace, it gives the carbide  $\text{CeC}_2$ . J. McC.

**Dextrose and Cerium Carbonates. A New Means of Induced Oxidation.** By ANDRÉ JOB (*Compt. rend.*, 1902, 134, 1052—1054. Compare Abstr., 1901, ii, 657).—Ceric carbonate, when shaken with air, gives cerium peroxide which can be recognised by its colour. If a solution of potassium arsenite be added, the red colour of the peroxide develops, but rapidly disappears when the agitation is stopped.

A concentrated solution of dextrose quickly reduces cerium peroxide. An alkaline solution of ceric carbonate is not oxidised by the air, but if dextrose be added cerium peroxide is produced. The dextrose induces the peroxidation of the cerium. Ceric carbonate does not oxidise potassium arsenite, but in presence of dextrose the arsenite is converted into arsenate. J. McC.

**Alloys of Aluminium.** By WILLIAM CAMPBELL and JOHN A. MATHEWS (*J. Amer. Chem. Soc.*, 1902, 24, 253—266).—The authors have studied the alloys of aluminium with lead, bismuth, cadmium, platinum, tungsten, nickel, tin, antimony, and copper.

The addition of 5—10 per cent. of platinum to aluminium causes no change of colour, but alloys containing 30—50 per cent. of platinum are distinctly yellow. By dissolving away the excess of aluminium, long, needle-shaped crystals are obtained of the composition  $\text{AlPt}_4$ .

From alloys containing 3—17 per cent. of tungsten, thin, monoclinic crystals of the composition  $\text{WAl}_5$  were obtained, and in one case hexagonal crystals of the composition  $\text{WAl}_7$  were isolated.

The addition of tin to aluminium causes a gradual depression of the freezing point to  $570^\circ$  when the alloy contains 74 per cent. of tin; a sudden fall then occurs to  $490^\circ$  with 80 per cent. of tin; from this point, the freezing point rises to  $550^\circ$  with 85 per cent. of tin, and then falls regularly to the eutectic point,  $229^\circ$ , when 99.52 per cent. of tin is present.

The paper is illustrated with diagrams and microphotographs.

E. G.

**Barium Aluminate employed as a Disencrusting Agent.** By GEORGES ARTH (*Bull. Soc. Chim.*, 1902, [iii], 27, 297—302).—For the

removal of calcium sulphate from boiler water on the commercial scale, the author finds that a quantity of barium aluminate less than is required by the equation  $\text{BaAl}_2\text{O}_4 + \text{CaSO}_4 = \text{BaSO}_4 + \text{CaAl}_2\text{O}_4$ , is sufficient to precipitate the sulphate; the resulting liquid, however, is not entirely free from dissolved salts, and is always found to contain lime in solution.

A. F.

**Compounds of Alumina and Chromium Sesquioxide.** By ANDRÉ DUBOIN (*Compt. rend.*, 1902, 134, 840—842).—Compounds of alumina with chromium sesquioxide present in a mixture of alumina and chromium sesquioxide can be analysed by fusing the mixture with potassium chlorate, which dissolves only the uncombined chromium sesquioxide. The analyses point to the existence of a compound,  $\text{Cr}_2\text{O}_3, 8\text{Al}_2\text{O}_3$ . The colour of the mixed oxides depends on the state of the alumina used. With calcined alumina, a much smaller proportion of chromium sesquioxide changes the original rose colour to green than when gelatinous alumina is used.

K. J. P. O.

**Crystallisation of Iron.** By FLORIS OSMOND and G. CARTAUD (*Chem. Centr.*, 1902, i, 848; from *Ann. Mines*, 17, 110—150; 18, 113—153).—When iron is heated from the ordinary temperature to its melting point, it undergoes two changes; the one taking place gradually between  $700^\circ$  and  $760^\circ$  and corresponding with the disappearance of the magnetic properties, the other occurring suddenly at  $860^\circ$ . Since the metal on solidification usually forms  $\gamma$ -iron, the octahedral crystals must belong to this form, although their internal structure corresponds with the  $\alpha$ -form, which is stable at the ordinary temperature. The crystalline form of  $\alpha$ - and  $\beta$ -iron can only be inferred from the appearance of the etched surfaces, and these show a cubical structure. Pure iron prepared at temperatures up to about  $800^\circ$  by reducing ferrous chloride with hydrogen usually separates in small hexahedra, but sometimes in tetrakis-hexahedra and rhombic dodecahedra. The hexahedra interpenetrate one another in the crystalline skeletons and crusts in the most various ways, but are always parallel. At temperatures from  $800$ — $1000^\circ$ , pure iron was prepared by reducing ferrous chloride with zinc vapour, usually in an atmosphere of nitrogen. The metal separated in hexahedra, often combined with octahedra and twinned on an octahedron face. The crystalline crusts obtained at these temperatures showed octahedral edges (twinning?), and their structure resembled that of the technically prepared  $\gamma$ -iron.

E. W. W.

**The Density of Aqueous Solutions of Ferrous Chloride.** By JOHN T. DUNN (*J. Soc. Chem. Ind.*, 1902, 21, 390).—The table on p. 401 is given, showing the amounts of ferrous chloride contained in solutions of various specific gravities.

Columns are also given showing the weights of ferrous chloride in 100 grams of solution and of the amounts of the crystallised salt ( $\text{FeCl}_2, 4\text{H}_2\text{O}$ ) contained in 100 c.c. and 100 grams of the solution. A second table gives similar information for solutions having sp. gr.

Specific gravity at 15°5'.	Grams of FeCl <sub>2</sub> in 100 c.c.	Specific gravity at 15°5'.	Grams of FeCl <sub>2</sub> in 100 c.c.
1·0459	5·19	1·2916	34·92
1·0892	10·27	1·3010	36·38
1·1255	14·64	1·3289	39·80
1·1385	16·08	1·3674	44·65
1·1688	19·73	1·4065	49·39
1·2103	24·95	1·4319	52·80
1·2528	30·16	1·4439	54·20
1·2625	31·55		

between 1·05 and 1·44, with a difference in their gravities of 0·01.

W. P. S.

**Germanium Hydride.** By E. VOEGELEN (*Zeit. anorg. Chem.*, 1902, 30, 325—330).—If germanium chloride is reduced with sodium amalgam, the hydrogen evolved, even when bubbled through sodium hydroxide solution, burns with a bluish-red flame, and deposits a mirror on a cold porcelain surface. Germanium hydride, to which this phenomenon is attributed, may be prepared also in Marsh's apparatus like antimony and arsenic hydrides; the mirror obtained by heating the tube through which the issuing gas passes is red in transmitted, green in reflected, light; it is soluble in sodium hypochlorite, difficultly so in hot hydrochloric acid; heating in air or with concentrated nitric acid changes the mirror into white germanic oxide, which, when acted on with hydrogen sulphide in hydrochloric acid solution, gives a white precipitate of germanium sulphide soluble in ammonium sulphide. When germanium hydride is passed through silver nitrate solution, a black compound of germanium and silver is precipitated; this, when treated with concentrated nitric acid, leaves a white residue of germanic oxide. The author has attempted to decide whether the formula of the hydride is  $\text{GeH}_2$ ,  $(\text{Ge}_2\text{H}_4)$ , or  $\text{GeH}_4$  by (1) analysing the germanium silver compound, (2) passing the germanium hydride over finely divided sulphur in a strong light, and comparing the amounts of germanium and hydrogen sulphides formed. The results, owing to the small quantity of material available, are not very consistent, but point to  $\text{GeH}_4$  as the formula of germanium hydride; this agrees with the formula of the tetraethyl derivative  $\text{GeEt}_4$ , prepared by Winkler (compare Winkler, *Abstr.*, 1886, 985; 1887, 1081).

Attempts to prepare tin hydride were unsuccessful, and in view of this the author characterises germanium as a non-metal. J. C. P.

**Sulphates of Bismuth.** By F. B. ALLAN (*Amer. Chem. J.*, 1902, 27, 284—288).—When acid bismuth sulphate,  $\text{Bi}_2\text{O}_3 \cdot 4\text{SO}_3$  (Adie, *Proc.*, 1899, 15, 226) is stirred with sulphuric acid of various concentrations until equilibrium occurs, the solid phase consists of this salt alone so long as the liquid phase contains from 60 to 90 per cent. of sulphuric acid; when this falls below 47·5 per cent., the separated solid consists of the salt  $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ , and the latter is stable until the concentration of the acid falls to 1·37; below this point, the solid phase is a mixture of the two salts  $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3$  and  $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ , until



the acid is reduced to 1.09 per cent., when  $\text{Bi}_2\text{O}_3\cdot\text{SO}_3$  remains, being stable in presence of water alone. No indication at any stage of the existence of the salt  $5\text{Bi}_2\text{O}_3\cdot 11\text{SO}_3\cdot 17\text{H}_2\text{O}$  was observed.

T. A. H.

**Preparation and Properties of Lead Chloro-, Bromo-, and Iodothiobismuthites.** By FERNAND DUCATTE (*Compt. rend.*, 1902, 134, 1061—1063).—*Lead chlorothiobismuthite* ( $\text{PbS}\cdot\text{Bi}_2\text{S}_3\cdot 2\text{BiS}\cdot\text{Cl}$ ) is produced by heating a mixture of equal parts of lead chloride and bismuth sulphide to the fusion point in a current of carbon dioxide. It is obtained in long crystals of sp. gr. 6.42, which are quite stable in the air and insoluble in water. It oxidises at a red heat and is decomposed by boiling water. With acid, it gives hydrogen sulphide. The corresponding *bromothiobismuthite* (sp. gr. 6.50) and *iodothiobismuthite* (sp. gr. 6.59) are obtained in the same way and closely resemble in appearance and properties the chlorothiobismuthite.

J. McC.

**Action of Selenic Acid on Gold.** By VICTOR LENHER (*J. Amer. Chem. Soc.*, 1902, 24, 354—355).—When gold is treated with hot concentrated selenic acid, it dissolves with liberation of selenium dioxide and formation of a reddish-yellow solution of *auric selenate*,  $\text{Au}_2(\text{SeO}_4)_3$ ; the action begins at about  $230^\circ$ , but proceeds more readily at  $300^\circ$ . The selenate forms small, yellow crystals; it is insoluble in water but soluble in sulphuric, nitric, or hot selenic acid. By the action of hydrochloric acid on it, chlorine is evolved and auric chloride and selenious acid are produced. It is decomposed by heat with production of metallic gold. On exposure to light, it becomes dark green and afterwards bronze-coloured.

E. G.

**Naturally Occurring Telluride of Gold.** By VICTOR LENHER (*J. Amer. Chem. Soc.*, 1902, 24, 355—360).—When a solution of auric chloride is added to tellurium, gold is deposited and tellurium tetrachloride is produced.  $4\text{AuCl}_3 + 3\text{Te} = 4\text{Au} + 3\text{TeCl}_4$ . A similar reaction takes place with solutions of silver salts. Selenium also causes the precipitation of gold from solutions of its salts. The natural tellurides (calaverite, sylvanite, coloradoite, kalgoorlite, and nagyagite) behave like tellurium itself in precipitating gold from a solution of auric chloride.

Attempts to prepare gold telluride artificially were unsuccessful. The experiments of Brauner (*Trans.*, 1889, 55, 391) on the synthesis of gold telluride were repeated. The product obtained by heating gold with tellurium in an atmosphere of carbon dioxide is of inconstant composition and reduces auric chloride. If hydrogen telluride is led into a solution of auric chloride, gold is precipitated.

It has been shown (this vol., ii, 316) that when tellurium is treated with sulphur monochloride, tellurium tetrachloride is produced; the natural tellurides behave in a similar manner, gold being left as a residue.

These facts seem to indicate that the natural tellurides are not to be regarded as true chemical compounds.

E. G.

## Mineralogical Chemistry.

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The Cerargyrite Group (Holohedral-cubic Silver Haloids). By GEORGE T. PRIOR and LEONARD J. SPENCER) *Min. Mag.*, 1902, 13, 174—185).—The results of the qualitative examination of twenty-eight specimens, from various localities, and the following quantitative analyses indicate that chlorargyrite, embolite, bromargyrite and iodobromite cannot be sharply divided into species as is done in modern text-books, but that they pass indefinitely into each other and form an isomorphous group the general composition of which is represented by the formula  $\text{Ag}(\text{Cl}, \text{Br}, \text{I})$ . There is no definite mineral with the composition,  $2\text{AgCl}, 2\text{AgBr}, \text{AgI}$ , to which the name iodobromite was given; for cerargyrites containing all three halogens in variable proportions, the name *iodembolite* is proposed, but in these the iodine cannot exceed the amount given by the ratio  $\text{Cl} : \text{Br} : \text{I} = 1 : 1 : 1$ . Analysis I is of orange-yellow cubo-octahedra of iodembolite from Chañarcillo, Chili; II, III, and IV are of material of which the colour is orange-yellow, greenish-yellow and pale greenish-grey respectively, from Broken Hill, New South Wales.

	Ag.	Cl.	Br.	I.	Total.	Sp. gr.	Approximate formula.
I.	60·37	7·11	22·35	10·39	100·22	6·17	$5\text{AgCl}, 7\text{AgBr}, 2\text{AgI}$
II.	56·93	1·96	32·22	8·77	99·88	6·31	$5\text{AgCl}, 40\text{AgBr}, 7\text{AgI}$
III.	67·28	14·36	15·85	2·35	99·84	5·82	$20\text{AgCl}, 10\text{AgBr}, \text{AgI}$
IV.	66·91	13·20	19·71	0·16	99·98	5·66	$3\text{AgCl}, 2\text{AgBr}$

The general characters of the group are summarised as follows: Holohedral-cubic; common forms, the cube and octahedron; twinning, on an octahedral plane, rare. Cleavage, none; fracture, uneven to sub-conchoidal. Tough and sectile;  $H = 2\frac{1}{2}$ . Sp. gr. variable, depending on chemical composition (the pure chloride has the sp. gr. 5·556). Lustre vitreous to resinous; translucent. The colour also varies with the composition, being grey or colourless in the pure chloride, greenish-grey in the pure bromide and chlorobromides, and greenish-yellow to orange-yellow when all three halogens are present.

The results of this and a previous paper (Abstr., 1901, ii, 394) show that silver iodide may crystallise under one or other of the following four conditions. At temperatures below  $146^\circ$  (assuming atmospheric pressure), the pure iodide crystallises as hemimorphic-rhombohedral iodyrite, whilst above this temperature tetrahedral-cubic crystals are formed; it may also enter, to a certain extent, into isomorphous mixture with holohedral-cubic silver chloride and bromide (cerargyrite); or, again, may form tetrahedral-cubic crystals of the double salt  $4\text{AgI}, \text{CuI}$  (miersite).

L. J. S.

Baumhauerite, a New Mineral; and Dufrenoyssite. By RICHARD H. SOLLY, with an analysis by HENRY JACKSON (*Min. Mag.*, 1902, 13, 151—171).—The new mineral, *baumhauerite*, closely resembles in appearance the other sulpharsenites of lead which occur in

the crystalline dolomite of the Binnenthal in Switzerland. The crystals are monoclinic with numerous forms, and there is a perfect cleavage parallel to the orthopinacoid. The streak is chocolate coloured. Sp. gr. 5.330. Analysis gave:

Pb.	Sb.	S.	Total.
48.86	24.39	26.42	99.67

These numbers agree with those required for the formula  $4\text{PbS}, 3\text{As}_2\text{S}_3$ , which has previously been assigned to liveingite (Abstr., 1901, ii, 558), but it is now pointed out that the analysis of liveingite agrees more closely with the formula  $5\text{PbS}, 4\text{As}_2\text{S}_3$ .

A detailed crystallographic examination of dufrenoysite ( $2\text{PbS}, \text{As}_2\text{S}_3$ ), also from the Binnenthal dolomite, shows that this mineral crystallises in the monoclinic system and not in the rhombic as previously asserted.

L. J. S.

**Identity of Kilbrickenite with Geocronite: Analyses of Miersite, Marshite, and Copper-pyrites.** By GEORGE T. PRIOR (*Min. Mag.*, 1902, 13, 186—190).—Kilbrickenite, from the Kilbricken Mine in County Clare, has usually been considered to be a distinct mineral species with the formula  $6\text{PbS}, \text{Sb}_2\text{S}_3$ , but a study of the literature suggests its identity with geocronite. A new analysis of the original massive material gave the results under I, agreeing with the formula  $5\text{PbS}, \text{Sb}_2\text{S}_3 + 5\text{PbS}, \text{As}_2\text{S}_3$ , which represents a double salt as recently suggested for geocronite (this vol., ii, 211):

	Pb.	Sb.	As.	S.	Total.	Sp. gr.
I.	68.49	9.13	4.59	17.20	99.41	6.45

Miersite and marshite (Abstr., 1901, ii, 394), from Broken Hill, New South Wales, now analysed for the first time, gave the results under II and III, agreeing with the formulæ  $4\text{AgI}, \text{CuI}$  and  $\text{CuI}$  respectively:

	Ag.	Cu.	I.	Total.	Sp. gr.
II.	38.17	5.64	56.58	100.39	5.640
III.	1.19	32.35	65.85	99.39	5.590

Copper-pyrites from Wheal Towan, St. Agnes, Cornwall, gave the results under IV agreeing with the usual formula  $\text{CuFeS}_2$ . The crystals were analysed on account of their unusual habit, being of pseudo-cubic symmetry as the result of twinning, and in this respect resembling the crystals of stannite recently described (Abstr., 1901, ii, 392).

	Cu.	Fe.	S.	Total.	Sp. gr.
IV.	33.60	30.92	34.90	99.42	4.17

L. J. S.

**Crystalline Development of Calaverite.** By G. F. HERBERT SMITH, with analyses by GEORGE T. PRIOR (*Min. Mag.*, 1902, 13, 122—150).—A detailed crystallographic description is given of calaverite from Cripple Creek, Colorado. The morphological development of the faces is in complete agreement with monoclinic symmetry, but when the crystals are referred to this system, as is done by

Penfield and Ford (this vol., ii, 28), the indices are exceedingly complex. The faces, although lying in zones, cannot be referred to a single space-lattice, and, in fact, there appear to be in all five distinct lattices, which are incongruent but not independent, the prism-zone being common to all. The principal and also the second lattices have triclinic symmetry, and a third is monoclinic. The intermingling of material of different structures indicates that the crystals are not homogeneous, and this heterogeneity is further suggested by certain crystallographic relations of calaverite to sylvanite and krennerite when considered in connection with the absence of cleavage and the extreme brittleness of the calaverite crystals. Four types of twinned crystals are described.

The following analyses, made on crystals, agree approximately with the formula  $\text{AuTe}_2$ :

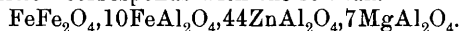
	Au.	Ag.	Te.	Total.	Sp. gr.
I.	41.66	0.77	57.87	100.30	} 9.155
II.	41.90	0.79	56.93	99.62	

L. J. S.

**Gahnite from Färila, Sweden.** By HERMAN HEDSTRÖM (*Jahrb Min.*, 1902, i, Ref. 165; from *Geol. För. Förh.*, 1901, 23, 42).—Crystals of gahnite, in association with iron-pyrites, copper-pyrites, and pyrrhotite, occur embedded in quartz-veins in a grey, garnetiferous gneiss at the Snuggens Copper Mine in the parish of Färila, Helsingland. The octahedral crystals are frequently twinned according to the spinel-law and measure up to 2 cm. across; they are black to blackish-green and have a vitreous to greasy lustre; splinters are translucent with a bottle-green colour; the streak is light green. Analysis gave:

$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{ZnO}$ .	$\text{MgO}$ .	$\text{SiO}_2$ .	$\text{CaO}$ .	Total.	Sp. gr.
55.85	9.44	32.11	2.47	0.12	trace	99.99	4.39

This composition corresponds with the formula



The other localities for zinc-spinel in Sweden are enumerated.

L. J. S.

**Calcite Crystals from Gräsberg, Sweden.** By MATS WEIBULL (*Jahrb. Min.*, 1902, i, Ref. 172; from *Geol. För. Förh.*, 1900, 22, 19—27).—A description is given of large crystals of calcite, which occur in crevices and druses in the iron-ores of Gräsberg, in Dalarne. The crystals have varied considerably in form at different periods of their growth, the earlier forms being marked out by enclosures of chlorite, göthite, &c. In order to determine whether this variation in form is due to differences in chemical composition, analyses were made of material from different portions of the crystals; no definite conclusion was, however, arrived at, although the development of certain crystal-faces does appear to depend on the presence of iron. The crystals contain, besides calcium carbonate,  $\text{MgCO}_3$ , 0.025—0.1 per cent., and  $\text{FeCO}_3$ , 0.033—0.75 per cent. (in the latter case, göthite was present).

L. J. S.

**Neotantalite; a New Mineral.** By PIERRE TERMIER (*Bull. Soc. franç. Min.*, 1902, 25, 34—38).—Minute, regular octahedra of the new mineral are obtained, together with cassiterite, as a heavy residue by washing the kaolin from Colettes and Échassières, dép. Allier, France. The crystals are of a pale yellow colour with a brilliant, almost adamantine lustre and resemble pyrochlore in appearance; they are optically isotropic;  $n$  1.9; sp. gr. 5.193; H 5—6. Analysis, by Pisani, gave the results under I; after deducting white mica and cassiterite, the composition of the mineral is given under II. Under the microscope, the crystals are seen to enclose, besides mica, also manganiferous hæmatite, so that the pure mineral probably does not contain more than 6 or 7 per cent. of FeO + MnO:

	Ta <sub>2</sub> O <sub>5</sub> .	Nb <sub>2</sub> O <sub>5</sub> .	FeO.	MnO.	SnO <sub>2</sub> .	Alkalis, (K, Na, Li).	SiO <sub>2</sub> .
I.	57.70	22.00	4.57	2.85	0.43	2.50	1.32
II.	60.58	23.10	4.80	3.00	—	2.31	—

	Al <sub>2</sub> O <sub>3</sub> .	MgO.	U.	H <sub>2</sub> O (at 1200°).	Total.
I.	1.43	trace	trace	6.30	99.24
II.	—	—	—	6.51	100.30

The new mineral is, chemically, quite distinct from the cubic tantalates and niobates of the pyrochlore group (pyrochlore, hatchetolite and microlite), and although it also differs considerably in composition from tantalite, it is considered to be a dimorphous form of this mineral. It is pointed out that certain of the crystal-angles of the rhombic tantalite approximate to those of cubic crystals.

L. J. S.

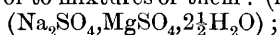
**A Peculiar Occurrence of Salts in the Magdeburg-Halberstadt Basin.** By K. KUBIERSCHKY (*Sitzungsber. Akad. Wiss. Berlin*, 1902, 404—413).—A single specimen, from Wilhelmsballe in the Stassfurt (more correctly Magdeburg-Halberstadt) salt district, consisting of colourless, and at first sight apparently homogeneous, material with an irregular fracture, gave in seven analyses the following extreme values:

K <sub>2</sub> SO <sub>4</sub> .	MgSO <sub>4</sub> .	Na <sub>2</sub> SO <sub>4</sub> .	H <sub>2</sub> O.	NaCl.
6.2—47.0	9.6—25.1	40.4—68.0	0.5—7.4	0.7—1.3

The curves obtained on plotting the results of these analyses indicate that the following salts are present in the mixture:

- (i) 3Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, to which the name *vanthoffite* is given;
- (ii) the triple salt, 3K<sub>2</sub>SO<sub>4</sub>, 4MgSO<sub>4</sub>, 6Na<sub>2</sub>SO<sub>4</sub>, 8H<sub>2</sub>O, which, however, may be a mixture of vanthoffite and K<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>,  $\frac{8}{3}$ H<sub>2</sub>O;
- (iii) (K, Na)<sub>2</sub>SO<sub>4</sub> (aphthitalite).

Eleven more analyses are given of material from a second and similar specimen which was separated into several portions according to small indefinable differences in appearance, and also by the aid of heavy liquids; these portions approximate in composition to the following mineral species or to mixtures of them: (i) löweite



(ii) vanthoffite; in the purest condition obtained, this is colourless with a vitreous lustre and coarsely crystalline structure, sp. gr. 2·7 (after deducting 10·2 per cent. of admixed sodium chloride), hardness rather over 3; (iii) apthitalite.

Attempts to artificially produce the triple sulphate noted above were unsuccessful; in one experiment, a salt having the composition  $2K_2SO_4, Na_2SO_4$  was obtained.

J. H. VAN'T HOFF, in an appendix (pp. 414—415), describes the means by which he prepared the salt  $3Na_2SO_4, MgSO_4$  (vanthoffite) artificially. Crystals of blödite ( $Na_2SO_4, MgSO_4, 4H_2O$ ), which at 22° are deposited from a solution containing equal molecular proportions of sodium and magnesium sulphates, when heated at 70° in the liquid lose some of their water and are transformed to löweite ( $Na_2SO_4, MgSO_4, 2H_2O$ , according to van't Hoff), whilst at a still higher temperature crystals of the anhydrous salt,  $3Na_2SO_4, MgSO_4$ , are formed. Other methods for the preparation of this salt are detailed.

L. J. S.

The Saline Sublimation Products of Vesuvius and the amounts of Molybdenum, Bismuth, Cobalt and Zinc therein. By EUGENIO CASORIA (*Chem. Centr.*, 1902, i, 828; from *B. Oss. Montcalieri*, [ii], 19, 86—89; 20, 2—7).—The crusts, stalactites, &c., formed since 1891 in the central crater in Atrio del Cavallo contain more potassium than sodium; molybdenum and zinc are also present in determinable amounts, but only traces of bismuth and cobalt. The composition of the sublimation products which have been formed since 1891 is very variable; they may consist of alkali chlorides alone or mixed with alkali sulphates and carbonates, or of mixtures of acid and normal alkali sulphates, together sometimes with free sulphuric acid or of complex salts. The products formed by the decomposition of the lava by the acid exhalations are found in close proximity to the sublimation products.

E. W. W.

Talc and Pyrophyllite Deposits in North Carolina. By JULIUS H. PRATT (*Jahrb. Min.*, 1902, i, Ref. 12—13; from *North Carolina Geol. Survey, Economic Papers*, 1900, No. 3, pp. 1—29).—Talc, of economic value, occurs in Cherokee and Macon counties as lenticular masses in marble at the contact of the latter with quartzite. The mineral is white, grey, or dark blue, and has a fibrous structure. Analyses by C. Baskerville of material from different mines are given under I—III. The marble contains tremolite, and near its contact with the quartzite has the composition of nearly pure dolomite. The talc is considered to be an alteration product of the tremolite, which itself was formed during the metamorphism of limestone to marble:

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	63·07	1·56	0·67	0·30	28·76	0·79	—	4·36	99·51
II.	61·35	4·42	1·68	0·82	26·03	0·62	—	5·10	100·02
III.	56·80	9·06	1·84	1·40	23·98	0·72	—	6·14	99·94
IV.	61·27	25·66	5·37	0·60	trace	0·83	0·11	5·86	99·70
V.	64·53	29·40	0·67	trace	trace	0·28	trace	5·45	100·33
VI.	63·50	28·73	0·84	trace	trace	0·37	trace	5·85	99·29

Pyrophyllite is mined in Moore and Chatham counties, and under the trade name of agalmatolite is used in place of talc. It occurs as beds in pyrophyllite-schist. The pure material is soft and flaky, and varies in colour from green and yellowish-white to nearly white; there are also black varieties, but these are of no commercial value. Analyses by C. Baskerville are given of the black (IV), yellowish (V), and apple-green (VI) material.

In analysis IV,  $\text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O} = 1.08 : 4 : 1.12$ .

„ V, „ „ = 1.08 : 4 : 1.24.

L. J. S.

[Muscovite] from Haddam Neck, Connecticut. By HERBERT L. BOWMAN (*Min. Mag.*, 1902, 13, 97—121).—A description is given of each of the following minerals from a pegmatite vein at Haddam Neck, Connecticut: muscovite, lepidolite, tourmaline, apatite, microcline, albite, beryl, quartz, cookeite, fluor, microlite and columbite. There are three varieties of muscovite: (1) colourless, in large sheets up to two feet across; (2) greenish-white, occurring as a central core in crystals of lepidolite; (3) pink and fibrous, coating the exterior of the crystals of lepidolite, and, at first sight, appearing to be an alteration product of this. The muscovite of the second and third varieties is grown in parallel or twinned position on the lilac-coloured lepidolite, which itself also consists of two varieties, depending on whether the optic axial plane is parallel, or perpendicular, to the plane of symmetry. The pink muscovite consists of masses of fibres of rhombic section attached together in parallel or twinned positions, so that the whole mass can be cleaved across as a single crystal; analysis of this variety gave the following results:

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	MnO.	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{Li}_2\text{O}$	$\text{P}_2\text{O}_5$	F.	$\text{H}_2\text{O}$	O for F.	Total less
46.28	36.86	0.97	trace	10.63	1.41	0.26	0.09	0.38	4.38	101.10	O for F.

L. J. S.

Thomsonite and Apophyllite from Schiket (Colonia Eritrea). By GIOVANNI D'ACHIARDI (*Atti R. Accad. Lincei*, 1902, [v], 11, i, 251—254).—The author gives descriptions of specimens of (1) thomsonite, of the Farcelite variety, which has a hardness of about 5, a sp. gr. of 2.25, and gave on analysis the following numbers:

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	CaO.	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{H}_2\text{O}$	Total.
41.30	29.49	11.61	5.11	traces	13.32	100.83

(2) Apophyllite, of the tesselite variety, having a hardness of 5 and sp. gr. 2.2; scarcity of the material prevented an analysis being made, identification being based on qualitative tests, and on optical and crystallographic examination.

T. H. P.

Barylite and Cordierite. By MATS WEIBULL (*Jahrb. Min.*, 1902, i, Ref. 176—178; from *Geol. För. Förh.*, 1900, 22, 33—42).—A re-examination of Blomstrand's barylite shows that the indistinct crystals are rhombic with a prism angle of  $44^\circ 26'$ . The milk-white colour of the mineral, and the small amount of water (0.15 per cent.) it contains, are due to numerous fluid enclosures. Some of the optical

characters have been determined. Blomstrand's empirical formula,  $\text{Ba}_4\text{Al}_4\text{Si}_7\text{O}_{24}$ , is written graphically in accordance with Clarke's theory of the silicates to show a relation between barylite, cordierite, knebelite and muscovite.

Cordierite occurs as large, light-blue individuals in copper-pyrites, blende and hornblende at the Långfalls Mine, Grangårde, Dalarne. It encloses, to the extent of a few per cent., sillimanite, dark (organic?) grains, and the alteration products, muscovite, talc and kaolin. Analysis by L. Ramberg gave :

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{MnO}$ .	$\text{MgO}$ .	Loss at 300°.	Loss on ignition.	Total.
48.90	32.54	0.95	2.96	trace	11.46	0.77	1.65	99.23

Neglecting the water, as probably due to alteration, this gives the formula  $\text{R}''_2\text{R}'''_4\text{Si}_5\text{O}_{13}$ , which is written constitutionally as  $[(\text{Mg}, \text{Fe})(\text{Al}, \text{Fe})(\text{AlO})]_2(\text{SiO}_4)_2(\text{Si}_3\text{O}_8)$ .  
L. J. S.

**Kaolin** from near Spezia, Italy. By E. SALLE (*Jahrb. Min.*, 1902, i, Ref. 173 ; from *Atti Soc. Toscana Sci. Nat.*, 1900, *Proc. Verb.*, 12, 103—106).—The following analysis is given of kaolin from the neighbourhood of Spezia. It is known as terra bianca, and was formerly thought to be chalk ; it has been formed by the decomposition of "euphotite" :

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{H}_2\text{O}$ .	$\text{Fe}_2\text{O}_3$ , Alkalis.	Total.
48.65	35.20	2.79	0.65	11.30	[1.41]	100.00
L. J. S.						

**Composition of the Magma at Different Stages of an Eruption.** By H. ARSANDAUX (*Bull. Soc. franç. Min.*, 1901, 24, 466—472).—The following analyses are given of ejected bombs of pyroxene-andesite from Santorin. I is of a bomb ejected at the beginning of the eruption in 1866 ; II in 1867 ; and III at the end of the eruption in 1868, IIIa being of material from the external portion, and IIIb from the internal portion of the bomb. These analyses go to show that during the period of eruption there has been no important variation in the composition of the magma. Calculating from these analyses the amounts of magnetite, pyroxene, albite and anorthite, there remains for the glassy base little alumina and much silica :

	$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{Na}_2\text{O}$ .	$\text{K}_2\text{O}$ .	Loss on ignition.	Total.
I.	67.6	16.5	1.6	3.4	2.6	2.2	4.9	1.8	0.7	101.3
II.	66.0	18.1	1.2	2.9	2.2	2.2	4.0	4.2	0.7	101.5
IIIa.	66.1	17.6	1.7	3.7	3.1	2.1	3.9	1.6	0.9	100.7
IIIb.	67.3	17.2	1.4	3.2	2.5	2.0	4.7	2.1	1.1	101.5

L. J. S.



## Physiological Chemistry.

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**Viscosity of the Blood.** By RUSSELL BURTON-OPITZ (*Amer. J. Physiol.*, 1902, 7, 243—260).—The average viscosity coefficient of frog's blood at 20° is 1300, of tortoise blood 1285, of rabbit's blood at 37°, 1350. The viscosity of frog's and tortoise's blood varies inversely as the temperature, a rise of 5° producing a rise of about 200 in the coefficient; thus at 37° it reaches 1700 in the frog and 1800 in the tortoise. The average viscosity of blood-serum at 20° is 1800. The viscosity coefficients of normal living blood vary widely, whilst those of the serum vary but little; the changes are therefore largely dependent on the solid elements of the blood. The specific gravity of frog's blood is altered by changes in the temperature in which the animal is placed; it is increased by potassium oxalate, curare, and deep etherisation, and diminished by defibrination. As similar changes are observed in the viscosity, considerable variations in the specific gravity may be taken as an index of variations in the viscosity. W. D. H.

**The Spleen and Blood Corpuscles.** By DIARMID NOËL PATON, G. LOVELL GULLAND, and J. S. FOWLER (*J. Physiol.*, 1902, 28, 83—106).—The number and character of the red blood corpuscles going to and coming from the spleen are the same. The leucocytes, especially those of the polymorphonuclear variety, are diminished. Removal of the spleen has no influence on the number of blood corpuscles, except a slight fall in the proportion of eosinophile leucocytes; the proteids of the plasma are also unchanged. After hæmorrhage or hæmolysis, the regeneration of red corpuscles occurs as rapidly in animals without a spleen as in those with one. Injection of spleen extract does not cause an increase in the red corpuscles, such as injection of extract of red bone-marrow produces. In the animals examined (dog, cat, rabbit), the spleen cannot be regarded as a blood-forming organ. The leucocytes formed in the Malpighian corpuscles are not supplied in any large number to the blood which leaves the spleen. W. D. H.

**Coagulation of Blood in Marine Animals.** By FILIPPO BOTTAZZI (*Arch. ital. Biol.*, 1902, 37, 49—54).—Among invertebrates, it is only in the group of the decapod crustaceans that a true coagulation of the blood is observed. Previous injection of 'peptone' does not prevent the coagulation of the blood when it is shed; but both 'peptone' and potassium oxalate do so *in vitro*; to do this, very large quantities must be added. 'Peptone' prevents the coalescence of the cells, and probably preserves them from profound alteration. In Elasmobranch fishes, 'peptone' injected into the hepatic portal vein in the proportion of 0.5—0.8 gram per kilo. of body weight acts as in other vertebrates. W. D. H.

**Lipolytic Function of the Blood.** By MAURICE DOYON and ALBERT MOREL (*Compt. rend.*, 1902, 134, 621—623).—In the normal blood of dog and horse kept aseptically at 37° in the presence of oxygen, the ethereal extract diminishes, but there is no simultaneous appearance of glycerol, fatty acids, or soaps, nor any change in the reaction of the blood. This action takes place mainly in the corpuscles; the change in the serum is very slight. W. D. H.

**Effects on the Constituents of the Blood, of Intravascular Injection of Hypertonic Salt Solutions.** By S. A. VAN LEER (*Zeit. Biol.*, 1902, 43, 52—66).—The investigation aimed at ascertaining whether in the elevation of the osmotic pressure of the blood produced by injecting hypertonic solutions of sodium sulphate, the proteids and the salts (sodium chloride and carbonate), work together so as to produce compensation by going out of the blood, as Hamburger states. This is answered in the negative. W. D. H.

**The Action of Lecithin on the Formed Elements of the Blood.** By HENRI STASSANO and F. BILLON (*Compt. rend.*, 1902, 134, 318—321).—Recent observations have shown that lecithin acts favourably on nutritive processes, being an easily assimilable form of phosphorus compound. The present experiments on rabbits show that intravenous injection of lecithin prepared from eggs increases the number of red blood corpuscles, and increases their resistance to certain saline solutions. It also increases the number of leucocytes, particularly of the mononuclear variety. W. D. H.

**Electrical Resistance, Index of Refraction, and Rotatory Power of Normal Serum.** By DONGIER and LESAGE (*Compt. rend.*, 1902, 134, 834—835).—Blood serum from healthy animals and men was examined; the electrical resistance at 16° varied from 93 to 103 ohms in animals, 100 to 300 in man; this is in proportion to the amount of inorganic salts; the refractive index varied from 1.3462 to 1.3503; the rotatory power from 1°14' to 2°11'. W. D. H.

**An Experimental Abnormality of Metabolism.** By HERMANN HILDEBRANDT (*Zeit. physiol. Chem.*, 1902, 35, 141—152).—Administration of large quantities of dextrose to rabbits produces an acute toxic condition, which can be hindered by giving calcium carbonate, whereby the reaction of the urine becomes alkaline. Glycuronic acid is an oxidation product of dextrose, and administration of large amounts of glycuronic acid causes an increased excretion of oxalic acid (P. Mayer, *Deut. med. Woch.*, 1901, Nos. 16 and 17). The poisonous symptoms referred to are due to an increased formation of oxalic acid; this acid appears in large quantities in the urine after abundant carbohydrate nutriment, but this is lessened by giving calcium carbonate. Lactose does not produce the same result. Oxaluria is a common symptom of diabetes in man; the administration of chalk is recommended. W. D. H.

**Purine Derivatives in Human Fæces.** By MARTIN KRÜGER and A. SCHITTENHELM (*Zeit. physiol. Chem.*, 1902, 35, 153—163).—In the course of 42 days, the following quantities of bases were found in the fæces of a man: guanine 2·363, adenine 1·88, xanthine 0·112, hypoxanthine 0·3, a total of 4·655, or a daily average of 0·11 gram; this is about three times the amount passed in the urine. W. D. H.

**Duodenal Digestion of Proteid.** By CARLO FERRAI (*Pflüger's Archiv*, 1902, 89, 527—546).—If proteid matter (cubes of coagulated albumin) is introduced into the duodenum of a dog in full digestive activity and the animal is then killed, the proteid is digested. The greatest intensity of digestion occurs in the first hour after death; it then rapidly falls, and practically ceases at the ninth hour. This is not due to the cooling of the corpse, but to other undetermined factors. The external temperature makes little or no difference. If the digestive processes are thrown into action by a meal given previously to the operation above described, the digestive action on the albumin cubes rises after death, and reaches a maximum  $2\frac{1}{2}$  hours later. If so much as four hours intervene between the preliminary meal and death, the digestive processes are weaker. The action appears to depend on the absolute quantity of active ferment, not on its concentration. The duodenal contents of an unfed animal have a digestive action on proteids. W. D. H.

[**Rôle of the Bile in Saponification.**] By EDUARD PFLÜGER (*Pflüger's Archiv*, 1902, 90, 1—32).—A method for estimating soaps and fatty acids in the presence of bile is described. Mixtures were used containing stearic and oleic acids, bile, and sodium hydroxide solution (1 per cent.); the amount of fatty acid in the form of soap subsequently varies from 53 to 65 per cent. Approval is expressed of Pawloff's idea concerning the self-steering action of intestinal digestion. The fatty acid liberated assists the hydrochloric acid from the stomach in stimulating the duodenum, and so producing a greater flow of pancreatic juice rich in steapsin; this resolves more and more fat, and the bile is mainly instrumental in rendering soluble the products of fat resolution. The author does not consider that Bayliss and Starling have as yet proved their contention that the link between duodenum and pancreas is not nervous. W. D. H.

**Action of Extracts of *Ascaris Lumbricoides*.** By ERNST WEINLAND (*Zeit. Biol.*, 1902, 43, 86—111. Compare this vol., ii, 155).—The previous research has shown that in the production of carbon dioxide and valeric acid in the metabolic processes of the round worm, *Ascaris*, a ferment action and not oxidation is the main factor concerned. In the present communication, the same action is studied in extracts squeezed out from the disintegrated worm, and the experiments recorded support the contention that the action is due to a ferment. W. D. H.

**Intestinal Absorption.** By E. WAYMOUTH REID (*J. Physiol.*, 1902, 28, 241—256).—The study of the absorption of weak solutions

of dextrose in the intestine, the mucous membrane being as normal as experimental procedure will admit, shows that the phenomena are such that a simple physical explanation is impossible. This corresponds with results previously obtained in the study of the absorption of serum. Probably with weak solutions of non-irritating substances the specific cell-action is the main factor, variable directly or indirectly according to changes in the physical environment. There is some evidence that chemical excitation may also play a part.

W. D. H.

**Absorption of Carbohydrates by the Rectum.** By FELIX REACH (*Chem. Centr.*, 1902, i, 824; from *Arch. exp. Path. Pharm.*, 1902, 47, 231—249).—From the standpoint of feeding *per rectum*, it is important to know whether carbohydrates are absorbed by the rectal mucous membrane. The method of experiment was to give enemata containing carbohydrates, and investigate the effect on the respiratory quotient, which approaches unity when abundant carbohydrate nutriment is given. The enemata contained 60 grams of dextrose, sucrose, maltose, or dextrin. The respiratory quotient rose, but more slowly and to a smaller extent than when the carbohydrate was given by the mouth. Starch enemata produced a still smaller and slower effect. In mouth feeding, there is an absolute rise in the respiratory gas exchange, due possibly to increased work of the digestive organs. This was not noticed in rectal feeding; glycosuria and dextrinuria did not occur.

W. D. H.

**Erepsin.** By OTTO COHNHEIM (*Zeit. physiol. Chem.*, 1902, 35, 134—140).—Erepsin acts rapidly on proteoses and peptones, and among the products of its action, ammonia, leucine, tyrosine, lysine, histidine, and arginine were identified. Erepsin acts also on protamines, and feebly on histon. It has no effect on any other of the native proteids investigated except caseinogen, which is rapidly split up. This opens up the interesting possibility that the suckling infant could digest its proteid nutriment in the absence of both pepsin and trypsin.

W. D. H.

**Chemical Composition of New-born Children.** By WILLIAM CAMERER, jun., SÖLDNER, and HERZOG (*Zeit. Biol.*, 1902, 43, 1—12).—Further analyses on the lines of the authors' previous work are given.

W. D. H.

**Osmotic Properties of Colloidal Solutions.** By BENJAMIN MOORE and WILLIAM H. PARKER (*Amer. J. Physiol.*, 1902, 7, 261—293).—Colloids in solution exert a definite osmotic pressure. This is not due to contamination with crystalloids. The only way of determining this is the direct one, variations in freezing or boiling points being so small. The pressure cannot be used to determine the mol. weight of colloids, for soaps by this method give *apparent* molecular weights 20 to 60 times too large. The physical constant which determines the osmotic pressure of a colloid is an osmotic unit or 'solution aggre-

gate' arising from the physical union or association of a variable number of molecules. This is four or five times as great for serum-albumin as for egg-albumin; that of serum-albumin is reduced to a fifth by alkalis. Even dilute solutions of sodium soaps form colloidal solutions in distilled water at temperatures from 50—70°, which do not diffuse through parchment paper. On cooling such solutions, hydrogels are obtained, which again yield solutions on heating. Such hydrogels are precipitated in granular form on keeping. Rapid cooling and increased strength of solution tend to the formation of hydrogels, whilst the opposite conditions tend to granule formation. These phenomena have their analogues in the passage of crystalloids from solution. The difference in the properties of the coagulable proteids may be due to different physical arrangements of chemical molecules to form different aggregates, and the complexity of the proteid molecule may be much more a physical than a chemical phenomenon. Protoplasm may be built up by a continuation of such a process; absorption by a cell may be governed by the formation of varying aggregates with the protoplasm already there, and similarly granule formation in the cells may also take place. The osmotic pressure of proteids probably takes no share in lymph production or absorption, for there is no evidence that capillary walls are impermeable to proteid, or that there is any appreciable difference in concentration in the two sides of the capillary wall. The cells of the membranes in the glomeruli of the kidneys probably act as secretory structures, for the differences in pressure are probably not sufficient to cause pressure filtration of a proteid-free filtrate, and are certainly many times too small to separate carbohydrate in this manner.

W. D. H.

**Formation of Lymph by the Liver.** By F. A. BAMBRIDGE (*J. Physiol.*, 1902, 28, 204—219).—The intravenous injection of moderate quantities of sodium taurocholate or of pure hæmoglobin leads both to an increased flow of lymph from the liver and increased metabolism in the liver cells. These substances constitute a class of lymphagogues additional to the two described by Heidenbain. The experiments support Asher's view that increased tissue activity causes an increase of lymph formation. Asher, however, goes too far when he says it is the sole cause. The statement of Asher that peptone, bile, and hæmoglobin are chologogues is not confirmed. The increased activity of the liver leads to a formation of crystalloid katabolic products, which enter the lymph by diffusion and raise its osmotic pressure, so increasing the flow of water by osmosis from the blood. The injection of ammonium salts sometimes causes an increased lymph flow, but the results are so inconstant that no conclusions are drawn as to its cause. The experiments were made on dogs. W. D. H.

**Effects of Potassium and Calcium Ions on Striated Muscle.** By W. D. ZOETHOUT (*Amer. J. Physiol.*, 1902, 7, 199—202).—Potassium ions produce a prolonged contraction of the striated muscle (gastrocnemius) of the frog; calcium ions, and to a lesser extent sodium ions, antagonise this action. This is almost the converse of

what obtains in the case of cardiac muscle, and has been previously described by Ringer and others. W. D. H.

**Lecithins.** By MAURICE BERNARD (*Chem. Centr.*, 1902, i, 854; from *Apoth.-Zeit.*, 17, 186—187. Compare Desgrez and Zaky, *Abstr.*, 1901, ii, 518).—The original paper contains a short description of the constitution, preparation, behaviour, and physiological action of lecithins. According to L. Vacheron (*La lécithine, nouvelle forme de la médication phosphorée*, 1902) the following amounts of lecithin are contained in 100 parts of the substances named: brain substance 11, liver 2.2, thymus 7.5, spermatozoa 1.50, red blood-corpuscles 0.72—1.86, milk 0.10, yolk of egg 6.80, peas 1.00, and lentils 1.00. Danilewsky finds that lecithins cause the red blood-corpuscles and hæmoglobin to increase, and promote growth. E. W. W.

**Ichthylepidin in the Scales of American Fishes.** By ERIK H. GREEN and R. W. TOWER (*Zeit. physiol. Chem.*, 1902, 35, 196—200).—The albuminoid called ichthylepidin by C. T. Mörner (*Abstr.*, 1898, ii, 85) is formed in the scales of a large number (32 varieties) of American teleostean fishes. The only teleostean in which it was not found is the sun-fish (*Mola mola*). It is present in the scales of the sturgeon, a ganoid, although, according to Mörner, it is absent from the scales of another ganoid, the gar-pike (*Lepidosteus osseus*). It was absent from the scales of four elasmobranchs. W. D. H.

**Pentoses in the Organism.** By GEORG GRUND (*Zeit. physiol. Chem.*, 1902, 35, 111—133).—Salkowski has shown that pentoses may appear in the urine as the result of metabolism, and Hammarsten that the nucleo-proteid of the pancreas yields a pentose on decomposition. It is now shown that other organs (liver, thymus, thyroid, spleen, kidneys, salivary glands, brain, and muscle) contain substances which also yield pentoses. The total amount of pentose obtained from the pancreas was 0.393 gram, that from all the organs just enumerated was 10.6 grams. W. D. H.

**Action of Rennin on Milk.** By ERNST FULD (*Beitr. chem. Physiol. Path.*, 1902, 2, 169—200).—The relationship between concentration of rennin and time of coagulation is found to be a constant one; other observations relate to the influence of temperature, and a large section of the paper is concerned with a discussion of theories concerning the action of the ferment. Milk curdling is regarded as a special case of the alternation between suspension and precipitation of a colloidal substance. During the change there is a development of heat, a slight elevation of the freezing point, but no notable change in the viscosity. W. D. H.

**Production of Uric Acid from Free Purine Bases.** By MARTIN KRÜGER and JULIUS SCHMID (*Zeit. physiol. Chem.*, 1902, 34, 549—565).—The conversion of hypoxanthine into uric acid in the animal system, appears to be a direct conversion, as it is not accompanied by leucotactic action, or by alterations in the phosphoric acid derivatives.

Adenine, xanthine, and probably guanine exert the same influence as hypoxanthine on the excretion of uric acid.

A small amount of the ingested adenine and xanthine contributes to a very slight increase in purine bases. J. J. S.

**Fatigue in Nerves.** By THOMAS GREGOR BRODIE, and WILLIAM D. HALLIBURTON (*J. Physiol.*, 1902, 28, 181—200).—By means of experiments similar to those made by other investigators on medullated nerves, the non-medullated nerves are also shown to be non-fatiguable. The block employed was cold, and the splenic nerves were those with which the greater number of the experiments were performed. Waller's hypothesis that the non-appearance of fatigue is due to the nutritive action of the fatty sheath is therefore not confirmed. Some of the nerves used especially those which are vaso-motor, exhibit what has been termed 'stimulation fatigue'; that is, the actual spot excited by a faradic current becomes less and less excitable and finally non-excitable. It is, however, still capable of conducting nerve impulses. The phenomenon is probably due to the injurious polarisation produced by the electric currents used. Non-medullated nerves are very sensitive to galvanic currents, and are rendered non-conducting and non-excitable. These nerves also are but little affected by chemical, thermal, and even mechanical excitation. They do not become acid even after many hours' activity. W. D. H.

**The Relation of Nitrogen and Carbon in Infants' Urine.** By VON OORDT (*Zeit. Biol.*, 1902, 43, 46—51).—Heubner and Rubner found in their experiments on puppies that the relative proportion of carbon in the urine was high. This is also true for children, especially when nourished on mother's milk; albumin and sugar are absent. W. D. H.

**Excretion of Ammonia in Human Urine.** By WILLIAM CAMERER, jun. (*Zeit. Biol.*, 1902, 43, 13—45).—The absolute amount of ammonia excreted is dependent on proteid katabolism, and thus on the amount of proteid nutriment. Growing individuals have a relatively high amount in the urine. In the course of the day urea excretion rises from the morning, reaching its maximum between 3 and 7 p.m. It then falls again, with a second small rise between 10 p.m. and 2 a.m. Ammonia excretion is high in the morning, reaches a minimum between 11 and 3, then rises and remains fairly constant until 2 a.m., when it rises again. The effects of diet and of the administration of acid and alkali are also given. In diabetic coma, the amount of ammonia in the urine rises considerably. W. D. H.

**Diuretic Action of Isotonic Salt Solutions.** By B. HAAKE and KARL SPIRO (*Beitr. chem. Physiol. Path.*, 1902, 2, 149—154).—Limbeck was the first to show that a solution of sodium chloride isotonic with the blood produces an increased flow of urine. Others subsequently showed that an isotonic solution of sodium sulphate produces a greater effect. The present experiments on rabbits show that solutions of sodium chloride, bromide, nitrate and sulphate, dextrose,

and sucrose, all isotonic with the blood, produce a diuretic effect. This is shown graphically in the form of curves. Of the substances mentioned, the effect of sodium chloride is least and most slowly developed. The activity of these substances as diuretics is not proportional to their toxicity.

W. D. H.

**The Work of Secretion in Diseased Kidneys.** By FRANZ SOETBEER (*Zeit. physiol. Chem.*, 1902, 35, 85—110).—The daily work of the kidneys in acute nephritis and amyloid disease is much smaller than in health. In interstitial nephritis, the work is about equal to that of the healthy kidneys, except that the excretion of uric acid is irregular; the actual amount of water is greater. In the two first-named diseases, the excretion of nitrogenous substances is fairly regular, still periods of retention alternate with periods of increased activity; this is very marked in the case of the mineral constituents of the urine; the retention of inorganic salts is not the cause of uræmia; this condition is probably related to the retention of organic substances, but the exact cause is not yet clear. In amyloid degeneration, the excretion of organic acids is increased.

W. D. H.

**Action of Curare on the Excretion of Carbon Dioxide and Nitrogen.** By OTTO FRANK and F. VON GEBHARD (*Zeit. Biol.*, 1902, 43, 117—124).—The present research was undertaken in view of contradictory results obtained by previous observers. The experiments were made on dogs; the carbon dioxide excretion fell from 11·15 grams per hour in the normal animal to 9·86—10·74 in the curarised animal, a fall of only 3·6 per cent. The excretion of nitrogen, however, fell enormously to only 25 per cent. of the normal.

W. D. H.

**Constitution of the Pancreas-Proteid-Pentose.** By CARL NEUBERG (*Ber.*, 1902, 35, 1467—1475).—Having shown (*Abstr.*, 1901, i, 539) that the pentose, which is found in certain pathological urines, is *r*-arabinose, the author has now investigated the pentose, which occurs associated with nucleoproteids in many organs. For this purpose, the nucleoproteid was extracted from ox-pancreas with boiling water, and to the extract hydrobromic acid was added; the mixture was boiled, and then neutralised with lead carbonate, which removed all coloured and oily products of hydrolysis. The filtrate was evaporated under reduced pressure, the residue extracted with alcohol, and the syrup obtained on evaporating off the alcohol oxidised with bromine water. From this solution of the acid obtained from the pentose, lead acetate precipitated lead bromide, but only after adding ammonia was the lead salt of *l*-xylonic acid thrown down. The acid was recognised by conversion into its brucine salt, and the characteristic double salt with cadmium bromide. The pentose of the pancreas-proteids is therefore *l*-xyllose.

K. J. P. O.

**Alcaptonuria.** By ERICH MEYER (*Chem. Centr.*, 1902, i, 364; from *Deut. Arch. klin. Med.*, 70, 443—467).—A case of alcaptonuria in a child is described; the secretion of homogentisic acid depends on



the proteid in the diet ; it is increased by giving plasmon. The well-characterised ethyl homogentisate is recommended for the identification of the substance.

W. D. H.

**Urobilin in Ascitic Fluid.** By CONRAD STICH (*Chem. Centr.*, 1902, i, 364 ; from *Münch. med. Woch.*, 48, 1751).—In a case of parenchymatous hæmorrhagic nephritis, urobilin was present in the ascitic fluid.

W. D. H.

**Arcus Senilis.** By J. HERBERT PARSONS (*Proc. Physiol. Soc.*, 1902 ; *J. Physiol.*, 28, 9—10).—The staining reactions and solubilities of the globules found in the substantia propria of the cornea in the area affected in *arcus senilis* indicate that they are fatty in nature. The reaction of fats to both osmic acid and sudan III is ascribed by others to members of the acrylic series ; the globules in question, however, although they are stained by the latter reagent, are unaffected by osmic acid.

W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Influence of Mineral Salts on the Respiration of Seeds during Different Periods of Germination.** By S. KRZEMIENIEWSKI (*Bull. Acad. Sci. Cracow*, 1902, 163—181).—In the first period of germination, mineral salts were found to be without effect, but after the maximum period of respiration had passed, addition of minerals resulted in a distinct acceleration of respiration, the assimilation of oxygen and the production of carbon dioxide being equally affected. When minerals are not added until the respiration has diminished considerably, owing to the reserved substances being much reduced in quantity, no accelerating action is observed, but the lessening of respiration is retarded.

The accelerating effect of mineral salts is due mainly to the potassium and the nitrates present; the other constituents are comparatively unimportant.

The amount of moisture in the substratum in which the plants are growing has a good deal of influence on respiration even when the air is saturated with moisture. The conclusion is drawn that increased root pressure is able to increase the respiration of the plant.

N. H. J. M.

**Do Germinating Seeds contain Peptonising or other Proteolytic Enzymes?** By THOMAS BOKORNY (*Pflüger's Archiv*, 1902, 90, 94—112).—Although the proteid matter of seeds during germination undergoes rapid solution, the non-discovery of peptone has hitherto been a difficulty, and researches directed to the isolation of a proteolytic enzyme have yielded contradictory results. An enzyme is present, and it appears to be of tryptic rather than of peptic nature.

This can be extracted from malt, and the name *peptase* is suggested. Leucine, tyrosine, asparagine, &c., were formed. It is possible that there are two enzymes, one that effects the solution of the globulin granules, and another that carries out the further decomposition which leads to the appearance of amino-acids.

W. D. H.

**Digestion of the Mannan of Orchid Tubers.** By HENRI HÉRISSEY (*Compt. rend.*, 1902, 134, 721—723).—The mannan of orchid tubers is converted into mannose by soluble ferments. The change can take place in the tubers themselves in proportion to the utilisation of reserve substance necessary for new growth. It can also be brought about by means of seminase from lucerne seeds.

N. H. J. M.

**Assimilation of Carbon by a Green Alga.** By P. G. CHARPENTIER (*Compt. rend.*, 1902, 184, 671—673).—*Cystococcus humicola* (Beyerinck, *Bot. Zeit.*, 1890) develops well in mineral solutions containing dextrose. It utilises the dextrose and also the carbon dioxide respired. Cultivations in closed vessels showed a production of carbon dioxide unaccompanied by any decided loss of oxygen. The presence of light is useful but not essential: the cells of *Cystococcus* produced in light are small and do not contain starch grains; they are coloured pale blue by iodine. In absence of light, the cells are large and full of large starch grains.

N. H. J. M.

**Effect of Temperature on Mineral Absorption by Etiolated Plants.** By GUSTAVE ANDRÉ (*Compt. rend.*, 1902, 134, 668—671).—Etiolated plants (maize and haricots), kept for 16 days at 30°, contained more total ash than similar plants kept at 15°; the difference was due to more silica having been taken up at the higher temperature.

The results relating to nitrogen did not show any very marked differences due to temperature, but as regards carbohydrates it was found that a distinctly greater production of vasculose took place at 30° than at 15°.

N. H. J. M.

**Rise of Colouring Matters in Plants.** By FRIEDRICH GOPPELS ROEDER (*Verhand. Naturforsch. Ges. Basel*, 1901, 14, 1—545).—See this vol., ii, 424.

**Chemical Reaction on the Surface of Roots.** By M. RACIBORSKI (*Bull. Acad. Sci. Cracow*, 1902, 51—54).—Leptomin was detected on the roots of every plant examined and probably occurs in all phanerogams; the quantity, however, varies a good deal. Maize, for instance, shows the reaction very plainly, whilst buckwheat only gave a very slight reaction. It was also detected in some above-ground portions of plants, but it is chiefly in the roots that the substance occurs.

The method employed for detecting leptomin is to lay the roots on paper saturated with an alcoholic solution of guaiacol (or  $\alpha$ -naphthol) and add diluted hydrogen peroxide; an intense blue (or violet) coloration is at once produced. The colour is produced when seeds are germinated on the prepared paper.

N. H. J. M.

**Sugar of Mahwa-Blossoms.** By EDMUND O. VON LIPPMANN (*Ber.*, 1902, **35**, 1448—1450).—A hard, crystalline sugar, resembling sucrose in appearance, was obtained from the syrup which is extracted from the blossom of *Bassia latifolia*. It was found, however, to be crystalline invert sugar.  
T. M. L.

**Constituents of the Pith of Maize and of Elder, and the simultaneous Occurrence of Araban and Xylan in Plants.** By C. A. BROWNE, jun., and BERNHARD TOLLENS (*Ber.*, 1902, **35**, 1457—1467).—The pith of both maize and elder gave the phloroglucinol reaction for pentose, and on distilling with hydrochloric acid the reactions for furfuraldehyde and methylfurfuraldehyde. In each pith, the fibre, ash, fat, proteid, and nitrogen-free extractive were estimated. There was evidence that a sugar resembling dextrose was also present in maize-pith.

The maize-pith was hydrolysed with 6 per cent. sulphuric acid, and the sugar (pentoses) isolated from the product by the usual methods (Widstoe and Tollens, *Abstr.*, 1900, i, 207). Xylose and arabinose were both isolated; xylan and araban are, therefore, both present in maize-pith. From elder-pith both pentoses were similarly isolated. From each source, the corresponding wood-gum was isolated by extraction with 5 per cent. sodium hydroxide; that from maize-pith had  $[\alpha]_D - 68.8^\circ$ , whilst that from elder-pith had  $[\alpha]_D - 36.8^\circ$ . By hydrolysis with calcium sulphite much cellulose can be extracted; as its presence cannot be demonstrated by the usual tests in the pith, the cellulose must be in combination with lignin, &c. From the fibre of the pith, a considerable quantity of cellulose was prepared by Cross and Bevan's chlorine method.

The authors have shown that beechwood-gum contains arabinose as well as xylose, and that cherry-gum contains xylose as well as arabinose.  
K. J. P. O.

**Composition of Orchid Tubers at Different Periods.** By KURT RAMMELBERG (*Bied. Centr.*, 1902, **31**, 256—257; from *Inaug. Diss. Erlangen*, 1899).—Invert sugar, sucrose, cellulose, and amylose were determined in young and old tubers of eleven varieties of orchids. The old tubers were found to contain the most cellulose, but generally they contain less invert sugar, sucrose, and amylose than the young tubers. The tubers contained (except in one case) more sucrose than invert sugar. The predominating constituent is amylose, especially the young in tubers.  
N. H. J. M.

**Sucrose in the Food Reserves of Phanerogams.** By ÉMILE BOURQUELOT (*Compt. rend.*, 1902, **134**, 718—720).—The results of the examination of the roots, tubers, and grains, &c., of different plants showed that sucrose was present in 18 cases out of 20. The conclusion is drawn that sucrose is necessary in the case of all phanerogams (compare Schulze, *Abstr.*, 1899, ii, 570).  
N. H. J. M.

**Action of Metallic Copper on Roots.** By KARL B. LEHMANN (*Chem. Centr.*, 1902, i, 765; from *Münch. med. Woch.*, **49**, 340).—On

growing beans, pumpkins, and peas in soil to which 7·5, 0·75, and 0·35 per cent. of copper had been added, it was found that the length of the roots was reduced, and that a number of short, hard, side branches were formed. The growth of the plants was decidedly injured by the presence of copper in the soil. N. H. J. M.

**Influence of the Sun on the Vine and Other Plants.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1902, [vii], 25, 433—452).—The grapes of a vine which has been injured by exposure to too intense sunlight are arrested in their development, the smallest grapes being those which have been most attacked by the sun's rays.

A long series of analyses of the proximate constituents of these imperfectly developed grapes indicates the connection between this arrested growth and the intensity of the sun's action. G. T. M.

**Conditions of Vegetation in High Yielding Vineyards.** By ACHILLE MÜNTZ (*Compt. rend.*, 1902, 134, 575—578).—To obtain the largest yields of grapes, it is necessary to apply very large amounts of manures. Under these conditions, there is a greater production of sugar in relation to the amount of manure applied than when the yield of grapes is only moderate. This is because the heavy application of manure tends to increase the yield of grapes more than that of the other organs.

Results are given showing that with the same leaf surface there may be very great differences in the amounts of sugar in the grapes, according to the quantity of manure, and it is supposed that in cases when the yield of sugar is low it is because the production of grapes was insufficient, the result being that the sugar was utilised in other ways. The important point would therefore seem to be to obtain a suitable relation of leaf to grapes in order to avoid, on the one hand, grapes poor in sugar, and, on the other, a loss of sugar owing to an insufficiency of grapes.

It is shown that leaving the grapes to mature as long as the climatic and soil conditions permit may result in a marked increase in the density of the must. N. H. J. M.

**Bananas.** By E. LEUSCHER (*Zeit. öffentl. Chem.*, 1902, 8, 125—134).—The following analyses of (1) green husks, (2) ripe husks, (3) unripe fruit, (4) ripe fruit (both without husks), (5) preserved bananas, and (6) banana-meal are given :

	Crude Water.	Crude protein.	Crude fat.	Crude fibre.	N-free extract.	Dex- trin.	Tan- nin.	Suc- rose.	Invert sugar.	Ash.
1.	70·00	2·02	4·51	9·89	8·26	—	—	—	—	5·32
2.	70·00	2·94	4·10	8·62	10·43	—	—	—	—	3·91
3.	70·50	3·94	0·14	0·39	—	19·10	2·63	2·18	—	1·12
4.	67·10	4·98	0·18	0·26	—	0·95	0·14	15·83	9·70	0·86
5.	25·20	6·80	0·25	0·36	65·59	—	—	—	—	1·80
6.	15·00	6·98	0·30	(5·90)	70·04	—	—	—	—	1·78

The results under crude fibre in the meal (6) include colouring matter and tannin. Only the quite green fruit, containing not more than traces of sugar, can be utilised for preparing meal. N. H. J. M.

**A Study of the Available Mineral Plant Food in Soils.** By CHARLES C. MOORE (*J. Amer. Chem. Soc.*, 1902, 24, 79—116).—The method employed consists in growing each crop in a variety of soils in large pots kept in a glasshouse so as to eliminate climatic conditions. The weights of produce are expressed in parts per 100,000, and the weights of nitrogen, ash, and ash constituents in the crop in parts per million of the soil. The cropping was oats and beans, each crop being followed in the same year by buckwheat.

Samples of the same soils are digested for 5 hours with dilute hydrochloric acid of different strengths, the bottles containing the soil being agitated at a fixed rate in a modified Wagner apparatus in an iron constant temperature chamber. On comparing the amounts of mineral substance dissolved by the dilute acid with the amounts taken up by the crop, it is possible to ascertain which strength of acid gives, with the majority of soils, the results most closely approximating to those obtained in actual growth. The strongest acid employed was  $N/10$  hydrochloric acid, and this dissolved from two to seven times as much as the crop took up. Very striking results were obtained with  $N/200$  acid. Of the 65 soils studied (including some Rothamsted wheat and barley soils), nearly all gave results indicating to a marked degree of accuracy the conditions as brought out in the crops.

In reference to the method of extracting with dilute citric acid, it is shown that it is important to extract at a constant temperature. It was found that a soil from which 0.012 per cent. of phosphoric acid was dissolved at  $30^{\circ}$  yielded 0.024 per cent. at  $40^{\circ}$ . The amount of potash dissolved was not affected by a difference of  $10^{\circ}$ . The amount of solvent (1 to 3 litres) and an increase in the percentage of citric acid, from 1 to 2, were without effect on the results.

The results recorded in the present paper refer only to oats, and it is probable that with other crops other strengths of acid will be found more suitable.

The method employed for soil sampling in the field is similar to that used at Rothamsted, except that the sampling irons are 6 inches deep and are round, being made from 7-inch wrought iron pipes.

For ascertaining the general composition of soils, 10 grams of each soil were digested in a reflux apparatus heated on a water-bath for 1, 5, 10, and 20 hours respectively with hydrochloric acid of sp. gr. 1.115. From the results obtained, the conclusion is drawn that 10 hours' digestion would give fairly approximate results. N. H. J. M.

**Vegetable Soils.** By THÉOPHILE SCHLOESING (*Compt. rend.*, 1902, 134, 631—635).—Four soils (50 grams each) were separated by levigation into eight portions, the water being poured off after 15 seconds, 1 and 5 minutes, 1, 5, and 20 hours, and 10 months. The final liquid was merely opalescent and was precipitated with a little nitric acid. The total substance, the phosphoric acid, and the iron sesquioxide were determined in each separation. The most striking results are the rapid increase in the amounts of phosphoric acid and iron oxide with the decrease in the size of the soil particles, and the constant relation between the ferric oxide and the phosphoric acid.

The results also indicate that the amounts of phosphoric acid and

ferric oxide in the colloidal clay resemble those in the very finely divided constituents of the soil. N. H. J. M.

**Studies in Nitrification.** By J. G. LIPMAN (*J. Amer. Chem. Soc.*, 1902, 24, 171—186).—The results of experiments in which 100 grams of soil, with 0.1 gram of ammonium sulphate, 8—12 c.c. of water, and 1 c.c. of soil extract (for inoculation), were kept in closed flasks, showed that in each case practically all the nitrogen was oxidised in 36 days, but that in some cases nitrification was either incomplete, or reduction to nitrites had taken place. The extracts of the soils, after being kept for 19 days, were found, in most cases, to contain less nitric nitrogen than when first prepared.

Similar experiments were made to ascertain the effect of sodium chloride, 0.01—0.1 per cent. of the weight of the soil. The results indicate that sodium chloride up to 3500 lb. per acre may retard, but does not entirely check, nitrification. Ferrous sulphate (0.01—0.1 per cent.) had very little effect, although the larger amounts seemed to retard nitrification somewhat. Linseed meal, 0.1 per cent., was more favourable to nitrification than 0.5 per cent., and with 3 per cent. of linseed meal only traces of nitric nitrogen were produced.

N. H. J. M.

**Value of the Nitrogen in Farmyard Manure and its Analytical Determination.** By THEODOR PFEIFFER, OTTO LEMMERMANN, R. RIECKE, and C. BLOCH (*Bied. Centr.*, 1902, 31, 236—239; from *Mitt. Landw. Inst. K. Univ. Breslau*, 1901, Heft 5, 189—219).—The varying effect of farmyard manure is attributed to the breaking down of sparingly soluble nitrogenous compounds by proteolytic ferments and to the simultaneous action of organisms which render insoluble the more soluble nitrogen compounds.

Attempts were made to determine the relative values of farmyard manure by means of the solubility of the nitrogen in pepsin, the results being compared with those obtained by vegetation experiments with the same manures in pots and on plots. It was found that the manure produced very different effects, according to whether the soil employed was heavy or light, and it seems, therefore, doubtful whether it will be possible by any analytical method to estimate the value of dung in the proposed direction. The results of pepsin digestion show, however, in some cases, a relation to the effects as observed in the vegetation experiments.

It was found that the manure generally lost nitrogen in soluble pepsin when kept; in some cases there was a gain. N. H. J. M.

**Ammonia in Meteoric Waters. Red Rain.** By ADOLFO CASALI (*Staz. Sper. agrar. ital.*, 1901, 34, 833—848).—The nitrogen, in the form of ammonia, was determined in thirty-five samples of the rain and snow, &c., collected in Bologna, from Jan. 15 to March 28, 1901. The maximum, minimum, and mean amounts of nitrogen per million were as follows:

	Nitrogen, as ammonia (mg. per litre).		
	Maximum.	Minimum.	Mean.
Mist.....	0·057	0·014	0·045
Hoar frost .....	0·045	0·022	0·023
Snow .....	0·008	0·002	0·005
Rain .....	0·012	0·001	0·005

The red rain, which fell during the night of March 10—11 (compare Abstr., 1901, ii, 322) contained 1·96 c.c. of dry substance in suspension, having the following percentage composition (sp. gr. 2·25) :

CaO.	MgO.	Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> .	SiO <sub>2</sub> .
4·87	2·22	34·98	57·75

The dust contains very little organic matter and was probably of meteoric origin. N. H. J. M.

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### Analytical Chemistry.

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Capillary Analysis, based on Capillary and Absorption Phenomena. Rise of Colouring Matters in Plants. By FRIEDRICH GOPFELSROEDER (*Verhand. Naturforsch. Ges. Basel*, 1901, 14, 1—545. Compare Abstr., 1899, ii, 572).—If one end of a strip of filter paper is immersed in a solution containing two or more dyes, the latter rise to different heights, giving a series of coloured zones. If these zones are cut off and extracted, the operation being repeated often enough, the dyes may ultimately be separated from each other. This process forms the basis of the author's extensive work on the above subject, in the course of which he deals with various kinds of capillary media (including plant stems) and various dissolved substances. J. C. P.

Stability of Potassium Tetraoxalate and Sodium Oxalate. By DUPRÉ, jun., and A. VON KUPFFER (*Zeit. angew. Chem.*, 1902, 15, 352—353).—Sodium oxalate, although difficult to procure in an absolutely pure condition, is preferable in volumetric analysis to potassium tetraoxalate which, according to the authors, suffers gradual deterioration by exposure to the air. L. DE K.

Estimation of Oxygen and Carbon Dioxide in Small Quantities of Blood. By JOSEPH BARCROFT and JOHN S. HALDANE (*J. Physiol.*, 1902, 28, 232—240).—The apparatus used is fully described and figured, and gives accurate results even although only about 1 c.c. of blood is used. It consists of a small glass vessel attached by tubing to a pressure gauge of narrow bore. It is so arranged that the oxygen in the blood can be liberated within it by potassium ferri-cyanide. By similar manipulation, with the use of tartaric acid instead

of ferricyanide, the carbon dioxide is subsequently liberated. In each case, the resulting increase of pressure is measured by the gauge, and from this the volume is calculated.

W. D. H.

**Colorimetric Estimation of Sulphur in Pig-Iron.** By W. G. LINDLAY (*Chem. Centr.*, 1902, i, 779; from *School of Mines Quarterly*, 23, 24).—Five grams of the sample are dissolved in hydrochloric acid, and the hydrogen sulphide is absorbed in aqueous sodium hydroxide. The alkaline solution is diluted to 250 c.c., and 5 c.c. of this are mixed in a Nessler tube with 1.5 c.c. of dilute sulphuric acid, 0.1 c.c. of a 2 per cent. solution of *p*-phenylenedimethyldiamine hydrochloride, and 0.05 c.c. of 10 per cent. ferric chloride. The mixture will assume a more or less strong blue colour due to methylene-blue. After 30 seconds, the colour is compared with solutions to which have been added 0.1, 0.2, or 0.3 c.c. of a solution of sodium sulphide containing 0.05 gram of sulphur per litre. Or a standardised solution of methylene-blue may serve as comparison liquid.

L. DE K.

**Estimation of Sulphur in Plants.** By GEORGE S. FRAPS (*J. Amer. Chem. Soc.*, 1902, 24, 346—348).—The following method is recommended. Five grams of the material are cautiously heated in a porcelain basin on the water-bath with 20 c.c. of concentrated nitric acid. As soon as all danger of frothing over has passed, the mixture is partially evaporated, 10 c.c. of a 5 per cent. solution of potassium nitrate are added, and the evaporation is continued to dryness. The residue is ignited, at first gently, and afterwards over a blast-lamp, until it becomes white. It is then dissolved in hydrochloric acid, evaporated to dryness, and heated for some time in an air-bath to render the silica insoluble. The residue is taken up with acidified water, filtered, and the sulphuric acid in the filtrate precipitated with barium chloride as usual. Igniting the plants in the presence of calcium acetate gave too low results.

W. P. S.

**A New Method for Titrating Free and Combined Sulphuric Acid.** By WOLF MÜLLER (*Ber.*, 1902, 35, 1587—1589).—A solution of benzidine hydrochloride is prepared by dissolving about 30 grams of the purified salt in a litre of water containing hydrochloric acid, and its acidity determined by titration against a standard solution of baryta or an alkali hydroxide, using phenolphthalein as indicator; as the salt is hydrolysed in aqueous solution, the acidity so determined is a measure of both the free and combined acid. An excess of the benzidine solution is then added to the hot solution, containing sulphuric acid or sulphate, to be estimated, when the whole of the latter is precipitated in the form of insoluble benzidine sulphate; the diminution in the total acidity of the mixture, determined by titrating an aliquot portion of the filtrate with the standard alkali, gives a measure of the benzidine removed, and hence also of the sulphuric acid precipitated. Results are given which show the degree of accuracy of the method, and indicate that the presence of hydrochloric or nitric acid is without prejudice to its use.

W. A. D.

**Kjeldahl's Method.** By CARL NEUBERG (*Beitr. chem. Physiol. Path.*, 1902, 2, 214—215).—The addition of sodium or potassium sulphide in fresh aqueous solution increases the volume of the liquid to be distilled and prolongs the process. Solid sodium thiosulphate is therefore recommended instead. The decomposition which occurs with the amido-mercuric sulphate is represented by the following equation:  $\text{Hg}(\text{NH}_3)_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} = \text{HgS} + (\text{NH}_4)_2\text{SO}_4 + \text{Na}_2\text{SO}_4$ . Control experiments show that the results obtained are identical with those obtained when an alkali sulphide is employed. W. D. H.

**A Nitrogen Apparatus.** By JOHN A. WESENER (*J. Amer. Chem. Soc.*, 1902, 24, 388—390).—The apparatus described is an arrangement or battery of distilling flasks for use in Kjeldahl's nitrogen process. The digestion with sulphuric acid is carried out in the same flask as is used for the distillation of the ammonia. A current of steam is employed to expel the latter. W. P. S.

**Estimation of Nitrogen in Urine Treated with Phosphotungstic and Hydrochloric Acids.** By WILLIAM CAMERER, sen. (*Zeit. Biol.*, 1902, 43, 67—85).—A critical and polemical discussion of methods of estimating urinary nitrogen. W. D. H.

**Commercial Liquor Ammonia, its Effect on Iron, its Impurities, and Methods for Estimating them.** By J. D. PENNOCK and D. A. MORTON (*J. Amer. Chem. Soc.*, 1902, 24, 377—388).—As the result of numerous experiments, it is stated that concentrated ammonia solution (28 to 28.5 per cent. of  $\text{NH}_3$ ) does not rust clean iron, and that it actually prevents its rusting, even in the presence of water, oxygen, or ammonium carbonate. The presence of free carbon dioxide is necessary for rusting to take place. Freshly rusted moist iron is acted on by concentrated ammonia solution, and the rusting continues for some considerable time, this being probably due to the rusty coat containing ferrous hydrogen carbonate. Old rusted iron is not attacked, the coat being ferric oxide and not ferrous hydrogen carbonate.

The impurities usually found in commercial liquor ammonia are carbon dioxide, tarry organic matter, and pyridine. The first may be determined by boiling 100 c.c. with a measured volume of *N* sodium hydroxide, precipitating the carbon dioxide with barium chloride, and filtering off the barium carbonate. The latter is then titrated in the usual way. Another method is to evaporate 100 c.c. of the ammonia solution down to about 20 c.c., after the addition of 5 c.c. of *N* sodium hydroxide. Fifty c.c. of cold boiled water, and a few drops of phenolphthalein solution are then added, the solution is cooled to 10°, and made neutral by running in *N*-acid until the last trace of pink colour is removed. Excess of *N*/10 sulphuric acid is then added, the solution boiled, and titrated back with *N*/10 sodium hydroxide. The amount of carbonate in the sodium hydroxide solution added in both methods must be separately estimated and allowed for. The organic (tarry) matter is estimated by boiling with *N*/50 potassium dichromate after making the solution

acid with dilute sulphuric acid. The excess of dichromate is then titrated back with standard ferrous sulphate solution. Pyridine is estimated by neutralising a known volume (100 c.c.) of the ammonia with sulphuric acid, using methyl-orange as indicator, and keeping the solution cool. The neutral mixture is then distilled. All the pyridine comes over in 70 c.c., the distillate being collected in 30 c.c. of cold water. Some ammonia also comes over and is removed by the addition of mercuric chloride to the distillate, using phenolphthalein as indicator. The latter is not coloured by pyridine, so that the pink colour is just removed when all the free ammonia has been combined. The solution is then filtered and titrated after the addition of a few drops of methyl-orange solution.

A table is given showing the percentage of ammonia in aqueous ammonia corresponding with any reading of the Baumé hydrometer between 24° and 27° at any temperature between 10° and 30°.

W. P. S.

**The Brucine Reaction for Nitrous Acid.** By GEORG LUNGE (*Zeit. angew. Chem.*, 1902, 15, 241—242. Compare this vol., ii, 288).—A further reply to Winkler (this vol., ii, 353). The author now acknowledges that when using a moderate amount of sulphuric acid the brucine reaction is also given by nitrous acid.

L. DE K.

**Reinsch's Test for Arsenic.** By EDGAR B. KENRICK (*J. Amer. Chem. Soc.*, 1902, 24, 276).—In the centre of a piece of sheet copper, a depression is punched an eighth of an inch deep and of the same diameter. The arsenic is deposited, as usual, on a piece of copper a few mm. in area. When dry, this is placed in the miniature crucible, which is then covered with a microscope cover glass cooled with a drop of water; a gentle flame is applied to sublime the arsenic. The cover glass is then microscopically examined for crystals of arsenious oxide, using a high power and proper illumination.

L. DE K.

**Common Errors in the Estimation of Silica.** By WILLIAM F. HILLEBRAND (*J. Amer. Chem. Soc.*, 1902, 24, 362—374).—The author confirms the statements of former investigators (see Abstr., 1894, ii, 366) that the methods in common use for rendering silica insoluble cannot be depended on. Silica is not rendered wholly insoluble by any number of evaporations with hydrochloric acid when followed by a single filtration, whatever the temperature employed may be. Two or more evaporations with intervening filtrations are necessary. Any silica which may pass into the filtrate in the presence of much aluminium or iron is not completely thrown down by ammonia or sodium acetate. Silica is also appreciably soluble in fused potassium pyrosulphate. The author also finds that ignition over the blast is needed to get the correct weight of the silica obtained.

W. P. S.

**Estimation of Carbon in the Presence of Osmium.** By GEORG VON KNORRE (*Zeit. angew. Chem.*, 1902, 15, 393—394).—The weighed substance (carbon-osmium fibre) is placed in a porcelain boat and

ignited inside a combustion tube in a current of oxygen. The gases evolved are freed from vapours of osmium tetroxide by passing them through a 150—200 c.c. Erlenmeyer flask containing 100 c.c. of a solution of ferrous sulphate (1:10) slightly acidified with sulphuric acid. As it is necessary to finally heat the solution to boiling to expel any dissolved carbon dioxide, the flask is attached to a reflux apparatus.

The carbon dioxide is, as usual, dried over calcium chloride and absorbed in a weighed potash apparatus. L. DE K.

**A New Form of Alkalimeter.** By CHARLES B. DAVIS (*J. Amer. Chem. Soc.*, 1902, **24**, 391—392).—The apparatus consists essentially of two conically shaped vessels, the bottom of one fitting into the top of the other by means of a ground-in joint. The upper flask is divided by a vertical partition into two chambers which are provided at top with glass stoppers. One chamber is filled with water and has at its lower end a bent capillary tube through which the water runs into the lower flask when the stopper is removed. The substance (carbonate) is weighed into the lower flask together with 1 gram each of salicylic and benzoic acids, the upper flask is fitted on, and after again weighing, the water is allowed to flow into the lower flask by removing the stopper of the water chamber. The liberated carbon dioxide passes through two bent capillary tubes in the second chamber of the upper flask, which has previously been partly filled with concentrated sulphuric acid. When the action is over, dry air, freed from carbon dioxide, is drawn through the apparatus, and the latter is again weighed to obtain the loss of weight due to carbon dioxide.

W. P. S.

**Estimation of Lithia in Lepidolite.** By W. J. SCHIEFFELIN and W. R. LAMAR (*J. Amer. Chem. Soc.*, 1902, **24**, 392—395).—The gently ignited chlorides of the alkalis, obtained in the usual way, are dissolved in 10 c.c. of hot water and 1 drop of hydrochloric acid. A little ammonia and ammonium oxalate are added and the solution is filtered into an Erlenmeyer flask of about 80 c.c. capacity. The contents of the flask are evaporated until crystallisation begins to take place (the volume will then be 1 or 2 c.c.); a few drops of water and hydrochloric acid are added and then 15 c.c. of amyl alcohol (b. p. 129—132°). The water is very cautiously boiled off and the volume of the amyl alcohol concentrated to about one-half. After cooling, the solution is filtered into a weighed platinum basin, and the residue is washed with amyl alcohol until free from lithia. The amyl alcohol is then evaporated off at a temperature below its boiling point. The residue in the basin is finally converted into sulphate, ignited, and weighed. Rubidium and caesium chlorides are practically insoluble in amyl alcohol.

W. P. S.

**Micro-chemical Reactions of Magnesium and Characterisation of Magnesium Ammonium Mellate.** By M. EMM. POZZI-ESCOT (*Ann. Chim. anal.*, 1902, **7**, 126—128).—In order to obtain a characteristic precipitate of ammonium magnesium phosphate for microscopical

purposes, two solutions are recommended: *A*, One gram of microcosmic salt, 4 grams of ammonium chloride, 2 grams of citric acid, 6 grams of ammonia, and 250 grams of water; *B*, 1 gram of microcosmic salt, 4 grams of ammonium chloride, 4 grams of citric acid, 10 grams of ammonia, and 250 grams of water.

When precipitated by *A*, the triple phosphate has the form of prisms with truncated edges. With *B*, the crystals are in the form of trapeziums or octahedrons.

By mixing an ammoniacal solution of a magnesium salt with ammonium mellate and concentrating the solution, crystals of ammonium magnesium mellate are formed which under the microscope have the appearance of large prisms the edges of which resemble enormous bacilli, or of long and slender prisms, the whole looking very much like potassium-palladium nitrite (*Abstr.*, 1900, ii, 271).

L. DE K.

**Rational Analysis of Clays.** By ALEXANDER SABECK (*Chem. Centr.*, 1902, i, 779—780; from *Chem. Ind.*, 25, 90—99).—Five grams of the sample are heated in a covered porcelain basin with 100 c.c. of water and 50 c.c. of sulphuric acid, the gas flame being at some distance from the bottom. In the presence of much organic matter, 15 c.c. of nitric acid are also added. The heating is discontinued when fumes of sulphuric acid are being given off, which is generally the case after about 4 hours. After diluting with water, the liquid is poured into a large beaker and the residue boiled for 5 minutes with 10 c.c. of a 33 per cent. solution of sodium hydroxide which is then also decanted into the beaker; the undissolved matter is treated several times in succession with 5 c.c. of hydrochloric acid, and with 10 c.c. of the alkali. The residue is finally brought on to a filter by means of dilute hydrochloric acid. The clear liquid in the beaker is carefully decanted and the remaining 50—100 c.c. which contain deposit are returned to the basin and subjected to the alternate treatment with acid and alkali, the clear acid and alkaline washings being, however, collected separately. Every particle of undissolved matter is finally collected on the same filter, which is then burnt in a weighed platinum dish. In the ash, quartz and felspar are separated by Seeger's method. The results are satisfactory for technical purposes.

L. DE K.

**Volumetric Estimation of Iron.** By WILHELM H. GINTL (*Zeit. angew. Chem.*, 1902, 15, 398—402, 424—434).—A review of the various methods proposed for the volumetric estimation of iron.

The following process is recommended by the author. The ferric solution is acidified with sulphuric acid, and introduced into a flask fitted with a Bunsen valve, and reduced by means of a spiral of palladium which has been charged with hydrogen either by heating it in a current of this gas at 100° or by electrolytical means. After heating for 1 hour and a half on the water-bath and cooling, the spiral (the end of which protrudes from the liquid) is withdrawn and the solution at once titrated with permanganate.

L. DE K.

**Estimation of Manganese in Iron.** By WILLIAM A. NOYES and G. HARRY CLAY (*J. Amer. Chem. Soc.*, 1902, 24, 243—245).—The reagents required are: a solution of ferrous ammonium sulphate containing 8.56 grams of this salt and 40 c.c. of 25 per cent. solution of sulphuric acid per litre, a solution of potassium permanganate, 1 c.c. of which represents 0.001 gram of iron or 0.0049 gram of manganese, and a solution made by dissolving 30 grams of crystallised sodium acetate in 30 c.c. of 30 per cent. acetic acid and 170 c.c. of water.

1.5 grams of the sample of iron are dissolved in 25 c.c. of nitric acid of sp. gr. 1.2, or 20 c.c. of this acid and 5 c.c. of hydrochloric acid of sp. gr. 1.2. After nearly neutralising the liquid with solution of sodium carbonate, an emulsion of zinc oxide is added until the iron begins to precipitate, and after 2 minutes an excess of zinc oxide is added. The whole is now diluted to 300 c.c., and 200 c.c. (= 1 gram of the sample) are mixed in a beaker with 20 c.c. of the sodium acetate solution and 40 c.c. of saturated bromine water. On boiling, the manganese separates as dioxide, which is then collected on a filter and washed. It is dissolved off the filter by means of 20 c.c. of the iron solution, and after thoroughly washing the filter, the filtrate is titrated with permanganate. The usual check is made and the difference in c.c. of permanganate represents the manganese. L. DE K.

**Volumetric Estimation of Molybdenum Steel.** By FRANCIS T. KOPP (*J. Amer. Chem. Soc.*, 1902, 24, 186—188).—About half a gram of the sample is dissolved in 2 c.c. of sulphuric acid of sp. gr. 1.58 and 12 c.c. of water; in the case of ferromolybdenum, this is dissolved in 12 c.c. of strong nitric acid followed by 2 c.c. of sulphuric acid. After evaporating until sulphuric acid fumes appear, 30 grams of fused potassium hydrogen sulphate are added, and the whole is fused for 15 minutes at a bright red heat. The fused mass is then dissolved in 500 c.c. of hot water, the liquid transferred to a litre flask, 100 c.c. of ammonia of sp. gr. 0.9 are added, and the whole made up to the mark. Five hundred c.c. of the filtrate are then mixed with 40 c.c. of sulphuric acid of sp. gr. 1.58 run through a Jones's zinc reductor, mixed with another 10 c.c. of sulphuric acid, and titrated with permanganate solution (1 c.c. = 0.003053 gram of iron). After allowing for impurities in the reagents, the molybdenum is found by multiplying the result by 0.71776.

When tungsten is present, 1 gram of the sample is dissolved in 25 c.c. of nitric acid of sp. gr. 1.20, 10 c.c. of hydrochloric acid are added, and the silica is rendered insoluble as usual. The dry mass is dissolved in 15 c.c. of hot hydrochloric acid, which will precipitate the tungsten as trioxide; when cold, the liquid is diluted to 100 c.c. and 50 c.c. of the filtrate are evaporated with 10 c.c. of sulphuric acid. The residue is then fused with 30 grams of potassium hydrogen sulphate as previously directed. L. DE K.

**Estimation of Molybdenum in Steel.** By GEORGE AUCHY (*J. Amer. Chem. Soc.*, 1902, 24, 273—275).—1.308 grams of the sample are dissolved in a large excess of nitric acid with addition of a little

potassium chlorate, the nitric acid is completely expelled by boiling and evaporation with hydrochloric acid, and the mass dried to render silica insoluble; a fresh quantity of hydrochloric acid is added and the solution evaporated until a scum begins to form. Five c.c. of hydrochloric acid diluted to 20 c.c. with water are now added and the mixture is heated until complete solution has taken place, when it is diluted to 50 c.c. The (filtered) solution is now slowly poured into a 300 c.c. flask containing 100 c.c. of water and 20 grams of sodium hydroxide, well shaken, and made up to the mark. After settling and filtering, 200 c.c. of the filtrate are collected, boiled down to 100 c.c., acidified with sulphuric acid, reduced with zinc, and titrated with permanganate. It is very important to make a blank test with steel free from molybdenum but containing the same amount of chromium as the sample, and to be careful to use exactly the same amount of hydrochloric acid.

L. DE K.

**Estimation of Thorium in Monazite-sand.** By EMIL BENZ (*Zeit. angew. Chem.*, 1902, 15, 297—309).—A review of the various methods used in the analysis of monazite-sand. The following process is finally recommended.

0.5 gram of the finely divided sample is mixed in a platinum crucible with 0.5 gram of sodium fluoride and then slowly fused with 10 grams of potassium pyrosulphate, the crucible being covered with a lid. When evolution of gas ceases, a faint red heat is applied for about 15 minutes, and when cold the mass is extracted with warm dilute hydrochloric acid. After filtering, the undissolved mass is boiled with a little strong acid, diluted with water, and again filtered. The mixed filtrate, measuring about 300 c.c., is partially neutralised with ammonia and then precipitated while boiling by adding 3—5 grams of solid ammonium oxalate. After remaining overnight, the precipitate is collected and the thorium estimated as follows. The oxalates are converted into nitrates by evaporation with fuming nitric acid, the residue is dissolved in 50 c.c. of water containing at most 1 c.c. of dilute nitric acid (1:10) and precipitated at 60—80° by adding 10 c.c. of hydrogen peroxide. The thorium peroxide is then converted by ignition into the oxide and weighed. A mere trace of cerium may be present which may be estimated colorimetrically.

L. DE K.

**Separation of Thorium.** By FLOYD J. METZGER (*J. Amer. Chem. Soc.*, 1902, 24, 275—276).—Preliminary experiments have shown that thorium may be quantitatively separated from cerium, lanthanum, or didymium by a double precipitation in a 40 per cent. alcoholic solution with fumaric acid. The application of the process to monazite will be tried, also the effect of other weak organic acids.

L. DE K.

**Estimation of Vanadium.** By DAVID T. WILLIAMS (*J. Soc. Chem. Ind.*, 1902, 21, 389—390).—From 1—2 grams of the ore are treated with about 6 c.c. of nitric acid until thorough decomposition has taken place. The solution is then evaporated to dryness, the residue heated with 4 c.c. of sulphuric acid to expel all nitric acid, diluted with hot water, and boiled. The lead sulphate is removed by



filtration, the filtrate is oxidised with 4 c.c. of nitric acid, and well boiled. After making alkaline with ammonia and re-acidifying with dilute sulphuric acid, the solution is cooled to 40° and titrated with a decinormal ferrous sulphate solution containing free sulphuric acid, using potassium ferricyanide as indicator. The amount of vanadium is found by multiplying the iron value of the ferrous sulphate solution by 0.914.

In the case of alloys, 0.5 gram is dissolved in *aqua regia* and evaporated with sulphuric acid as above. Copper has no detrimental effect on the analysis. W. P. S.

**The Peroxide Calorimeter as applied to European Coals and Petroleum.** By SAMUEL W. PARR (*J. Amer. Chem. Soc.*, 1902, 24, 167—171).—Sodium peroxide is not a sufficiently strong oxidiser for the combustion of European coals or petroleum, but this can be remedied by the addition of potassium persulphate and tartaric acid. 0.5 gram of dried coal is mixed by means of a wire with 1.5 grams of a mixture of potassium persulphate and tartaric acid (2:1); to the whole is then added 12 grams of sodium peroxide. A blank experiment is made to ascertain the amount of heat developed by the oxidising mixture alone.

In the case of petroleum, 3 grams of sodium peroxide are introduced into the cartridge and on this is dropped 1/3 of a gram of petroleum, using a dropping pipette from a light weighing flask, the exact weight of the oil being found by difference. To this is now added 1.5 grams of the mixture of potassium persulphate and tartaric acid and the whole is well stirred with a wire so as to have an even mixture. Twelve grams of sodium peroxide are now added and the whole, after being well shaken, is ready for ignition by means of a hot soft iron wire, as usual. After allowing for the heat developed by the oxidising mixture, 73 per cent. of the remainder is due to heat of combustion and 27 per cent. to heat of combination of the chemical products.

L. DE K.

**Estimation of Essential Oils in Spices.** By CARL MANN (*Arch. Pharm.*, 1902, 240, 149—166).—The apparatus employed is figured in the paper. The spice is powdered coarsely and 20 grams of it are mixed with half the weight of coarsely powdered pumice and placed in a sort of test-tube. This tube has some perforations below and is fixed in the cork of a wider tube, which contracts below to a narrower tube which is fitted to a tin can serving as a boiler. The upper part of the test-tube is fitted with a drop-catcher still-head and connected with a long condenser. When the boiler is heated, the steam jackets the tube containing the spice and heats it; at the same time it blows through the perforations and carries with it into the condenser the oil contained in the spice. The distillation is continued until no more oil comes over; this requires 1½—2½ hours. The distillate, which amounts to 400—900 c.c., is collected in a flask of 1—1½ litres capacity, the neck of which is graduated at intervals of 25 c.c. It is shaken with a quarter of its weight of salt freed from impurities insoluble in water; when this has dissolved, 50 c.c. of "rhigolene" are

added (a light petroleum fraction boiling at 20—35°, obtained by fractionating "naphtha"); the whole is shaken for half-an-hour, and set aside 2 hours to settle. Distilled water is added cautiously until the aqueous solution reaches the lowest mark in the neck, and "rhigolene" added to replace the unavoidable loss by evaporation and make the layer of it reach to the mark 50 c.c. above. Half of this layer is removed with a 25 c.c. pipette to a conical flask, which has a side tube and a tube ground in at the neck, each fitted with a stopcock. Dried air is aspirated through this flask by means of a water-pump until the air expelled from the pump, which is driven over calcium chloride and then through a fine platinum jet against the top of a small bunsen flame, ceases to produce a small, luminous cone by its burning. The stopcocks are then closed, and the residual essential oil is weighed; its weight multiplied by ten gives the percentage of oil in the spice. Control experiments showed that on the average 0.0137 gram of oil is lost for every 0.5 gram that is weighed; this may be added as a correction.

The method was compared with those commonly employed for the estimation of eugenol (as benzoyl-eugenol), of benzaldehyde (as benzylidenephnylhydrazine), and of mustard oil (as silver sulphide, from the thiosinamine first formed); the results were satisfactory. Estimations of the essential oil in several spices were made in this way, in each case in duplicate; the difference between two corresponding estimations amounted usually to 1—4 per cent. of the whole amount of the oil, in one or two cases to 10—15 per cent.

For liqueurs, a similar method may be used. If only alcohol, water, and sugar are present in addition to the essential oil, 100 c.c. of the liqueur are diluted with five times the amount of water, the mixture saturated with salt, and extracted with 50 c.c. of rhigolene, the extract being treated as above. If resins, fats, chlorophyll, or "extractive substances" are present, the distillation apparatus is employed, the tube of it being packed with a mixture of purified cellulose, with half its weight of pumice, and 25 c.c. of the rhigolene extract run upon this; in the distillation, the resins, &c., remain in the cellulose.

For perfumed soaps, 20 grams, in fine shavings, are dissolved in 150 c.c. of water and 20 grams of 90 per cent. alcohol in a conical flask fitted to a reflux apparatus. The solution is cooled, neutralised accurately with dilute sulphuric acid, of which 1 drop is then added in excess, and saturated with salt; about 1.5 gram of tannin is added and a few small lumps of pumice, and the liquid is heated gently and steam blown through it in such a way that the volume is kept constant; the distillate is treated as already described.

For perfumes, the same method may be employed as for liqueurs, except that a smaller quantity, 5—10 grams, may be taken.

C. F. B.

**Chemical Analysis of Wine.** By MAURICE BERNARD (*Chem. Centr.*, 1902, i, 784; from *Pharm. Zeit.*, 47, 140).—The author recommends the following method as a rapid means of deciding whether wines may pass as genuine or ought to be detained for further investigation.

The extract is determined by the official (German) method. The total acidity is determined by titrating 25 c.c. of the sample with  $N/4$  potassium hydroxide, using azolitmin paper as indicator. The neutralised wine is then evaporated to 10 c.c., decolorised with animal charcoal, filtered, and again made up to 25 c.c. Twenty c.c. of this are then boiled for 3 minutes with excess of diluted Fehling's solution, the precipitated cuprous oxide is collected, washed, and dissolved in a little dilute nitric acid; after removing the acid by means of urea, potassium iodide is added, and the iodine set free by the copper solution is titrated as usual and calculated to invert sugar. For the estimation of the fixed acidity and the sucrose, 25 c.c. of the wine are evaporated nearly to dryness, the residue is redissolved in water, and titrated as before. The solution is now fully inverted by heating for 20 minutes on the water-bath with addition of 2 c.c. of 1 per cent. hydrogen chloride solution; the sugar is then again estimated. When determining the ash, it should be moistened a few times with water and gently re-ignited.

L. DE K.

**Estimation of Methoxyl with the Aid of Gregor's Washing-liquid.** By J. MOLL VAN CHARANTE (*Rec. Trav. Chim.*, 1902, 21, 38—41).—It is found that the use of a solution of arsenious oxide in aqueous potassium carbonate (Gregor, *Abstr.*, 1898, ii, 490), in place of the suspension of red phosphorus in water, recommended by Zeisel in the estimation of methoxyl groups, leads to loss of methyl iodide. Thus, in an analysis of methylglucoside, from 1 to 6 per cent. too little methoxyl was found by Gregor's method, whereas Zeisel's gave quite accurate results.

K. J. P. O.

**Estimation of Sugars in the Blood.** By RAPHAEL LÉPINE and BOULUD (*Compt. rend.*, 1902, 134, 398—400).—Extracts of blood are first examined by the polarimeter, and its reducing action on cupric salts is also estimated. A second estimation is made after the same extract has been heated at  $100^{\circ}$  for 3 minutes to destroy the combinations of glycuronic acid; a third estimation is made after fermentation with yeast, and a fourth after the action of invertin. Examples are given of the results obtained.

W. D. H.

**Colour Test for Wood-fibre.** By ALBERT KAISER (*Chem. Zeit.*, 1902, 24, 335).—Equal volumes of amyl alcohol, free from furfuraldehyde, and sulphuric acid are heated at  $90^{\circ}$  until there is a slight evolution of gas, and the reddish-green product is then cooled. Pure filter paper, when moistened with this reagent, turns red or violet, but paper containing wood-pulp turns first green and then a fine blue. The test is accelerated by gently warming in a current of air.

The colour is due to the formation of furfuraldehyde from the wood-pulp, which then gives Vitali's reaction with amyl-sulphuric acid.

L. DE K.

**Quantitative Separation of Hydrochloric and Hydrocyanic Acids.** By THEODORE W. RICHARDS and SIDNEY K. SINGER (*Amer. Chem. J.*, 1902, 27, 205—209).—The process given by the authors is

well adapted for the estimation of chlorides in commercial potassium cyanide. About 1.25 grams of the salt are dissolved in 400 c.c. of water and the solution placed in an untubulated 500 c.c. retort with its neck directed upward at an angle of 45°. The volume of the liquid should not be allowed to fall below 300 c.c. After adding 5 c.c. of sulphuric acid and boiling for 8 to 9 hours, all the hydrocyanic acid is expelled and the hydrochloric acid is then estimated in the residual liquid by means of silver nitrate.

If the amount of chlorine is very trifling, a 2 hours' boiling suffices. If it is desired to also estimate the hydrocyanic acid, the most convenient way would probably be to precipitate it as silver cyanide, allowing for the silver chloride precipitated at the same time.

L. DE K.

**Direct Titration of Uric Acid in Urine.** By I. RUHEMANN (*Chem. Centr.*, 1902, i, 784—785; from *Berl. Klin. Woch.*, 1901, 39, 27—29, 55—58).—The apparatus termed "Urikometer," consists of a glass tube carrying three marks. Carbon disulphide (about 20 drops) is added up to the first mark, and a solution containing 1.5 grams of iodine and 1.5 grams of potassium iodide dissolved in 15 grams of alcohol and 185 grams of water is added up to the second mark; the amount of iodine thus introduced equals 0.015 gram. The space between the second and third marks is occupied by a scale showing the quantity of uric acid per 1000 parts of urine. The sample to be tested is now added little by little with thorough shaking until the free iodine has been all absorbed as shown by the final bleaching of the carbon disulphide, and when the foam has subsided the scale is read off. In constructing this scale, urines have been used the uric acid of which was previously determined by means of the gravimetric (hydrochloric acid) method. The urine should be acid, and must be made so, if necessary, by addition of acetic acid, and albuminous matters should be precipitated by boiling. Urines very rich in uric acid must be suitably diluted; if very poor in acid, a weaker iodine solution must be employed.

L. DE K.

**Assay of Crude Cream of Tartar.** By P. CARLES (*Ann. Chim. anal.*, 1902, 7, 121—123).—Chancel's "casserole process" gives results which are sufficiently accurate for technical purposes, provided the temperature is kept for 12 hours at 15°; 1 litre of mother liquor then retains 5 grams of potassium hydrogen tartrate. When the temperature is different, the amount of dissolved matter also varies. Correction must be made for the solubility of potassium hydrogen tartrate in water. At 0°, 5°, 10°, 15°, 20°, 25°, and 30°, 1 litre of water dissolves respectively 3.2, 3.6, 4.0, 5, 5.7, 7.35, and 9 grams of this salt.

L. DE K.

**Relation of the Heat of Combustion to the Specific Gravity in Fatty Oils.** By H. C. SHERMAN and J. F. SNELL (*J. Amer. Chem. Soc.*, 1902, 24, 348—353).—The determinations of the heat of combustion and sp. gr. of the oils mentioned in the previous paper (*Abstr.*, 1901, ii, 431) have been repeated. The results show that in

fresh fatty oils the heat of combustion is a property quite as constant as the sp. gr., to which it bears a definite relation. Oxidation resulting from exposure to air decreases the heat of combustion to the same extent that it increases the sp. gr., whence it is inferred that the oxygen is taken up by direct addition and without essential change in the volume of the oil. On account of its close quantitative relations to the sp. gr. and ultimate composition, the heat of combustion is a useful factor in the study of the fatty oils. E. G.

**Temperature Reaction of Oils with Sulphuric Acid—Mau-mene's Test.** By H. C. SHERMAN, J. L. DANZIGER, and L. KOHNSTAMM (*J. Amer. Chem. Soc.*, 1902, 24, 266—273).—An acid is taken containing only 89—90 per cent. of hydrogen sulphate and this may be used for every kind of drying oil without having to employ diluents. The rise in temperature is multiplied by 100 and divided by the rise obtained with water as already proposed by Thomson and Ballantyne (*Abstr.*, 1892, ii, 547), the result being the specific temperature reaction.

The results obtained by the authors are a little lower than those obtained by Thomson and Ballantyne, although in the case of a few animal oils they are somewhat higher. The average figures are, for raw linseed oil 299, poppyseed oil 212, maize oil 163, cottonseed oil 152, rape oil 150, arachis oil 161, sesamé oil 143, almond oil 95, olive oil 90, castor oil 84, menhaden oil 333, cod-liver oil 270, seal oil 255, lard oil 85, sperm oil 102, and rosin oil 72. L. DE K.

**A Comparison of Methods Used to Determine the Iodine Values of Oils.** By F. W. HUNT (*J. Soc. Chem. Ind.*, 1902, 21, 454—456).—The conclusion arrived at is that the Hübl method can be replaced by either the Wijs (iodine trichloride dissolved in glacial acetic acid) or Hanuš (iodine monobromide dissolved in glacial acetic acid) processes. The Hanuš solution gave figures slightly higher than the Hübl figures in the case of fish oils, but not so high as those of Wijs. With seed oils, the results of all three methods agree closely. The use of carbon tetrachloride as a solvent in place of glacial acetic acid is not recommended. The Hanuš and Wijs solutions keep well, but with a slight decrease in strength. W. P. S.

**Use of the Bechi or Silver Nitrate Test with Olive Oils.** By L. M. TOLMAN (*J. Amer. Chem. Soc.*, 1902, 24, 396—397).—As nearly all olive oils give a brown coloration with the Bechi test, the author purifies the oil as follows before applying the test. Twenty-five c.c. of the oil are mixed with 25 c.c. of alcohol (95 per cent.), shaken, and gently heated. When the liquids have separated, the alcohol is removed, and the oil is then washed with 2 per cent. nitric acid and finally with water. Cotton-seed oil when so treated reacts with undiminished strength, whilst pure olive oils, which previously gave a brown colour, showed no reduction. W. P. S.

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## General and Physical Chemistry.

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**Refraction of Normal Salt Solutions.** By CARL BENDER (*Ann. Physik.*, 1902, [iv], 8, 109—122. Compare Abstr., 1899, ii, 621; 1900, ii, 461).—The previous investigations have been extended to sodium chloride solutions of  $N/2$ ,  $N$ ,  $2N$ ,  $3N$ ,  $4N$ , and  $4.5N$  concentration, and interpolation formulæ are given expressing the relation of the index of refraction to the temperature. These curves approach more and more the form of a straight line with rising temperature and increasing concentration. The dispersion, as measured by  $H_\gamma - H_\alpha$ , decreases somewhat as the temperature rises. The molecular refraction (Lorenz) of sodium chloride for the sodium line is found to be 9.273, whence the atomic refraction of sodium is calculated to be 3.493. Assuming that the density of sodium at  $15^\circ$  is 0.985, this would give 1.23601 as the index of refraction of metallic sodium for the sodium line.

J. C. P.

**The Constitution of Matter and Spectroscopy.** By B. EGINTIS (*Compt. rend.*, 1902, 134, 1137—1139).—The author's observations, combined with those of Schuster (*Phil. Trans.*, 1899, 193, 189) and Hemsalech, lead to the conclusion that the intensities of the different lines of a metal depend on the nature of the other metals with which it is mixed and on the nature of the medium across which the electric discharge takes place. Some lines of simple metals form groups, the variations in which are probably due to the variations in the constitution of the radiating particles and in the nature of the poles. There seems to be a relation between these groups and the groups of lines that have the same velocity. During the discharges, the metallic vapours show electrical properties which vary with the nature of the vapours and differ considerably from those of air. The utilisation of self-induction in electrical discharges across gases constitutes a method for examining the constitution of matter.

C. H. B.

**Nature and Constitution of the Spectra of the Aurora Borealis.** By HENRI STASSANO (*Ann. Chim. Phys.*, 1902, [vii], 26, 40—57).—The predominant rays of the spectra of the aurora borealis and the solar prominences are due to neon, argon, helium, and hydrogen, the luminosity being caused by those gases which are most volatile and the best conductors of electricity at temperatures near  $-200^\circ$  under very greatly diminished pressure (compare Liveing and Dewar, Abstr., 1901, ii, 213).

G. T. M.

**A Simple Trough for Light-Filters.** By CHR. WINTHER (*Ber.*, 1902, 35, 1976—1977).—A block of wood ( $6 \times 6 \times 2$  cm.) is pierced by a cylindrical hole (3 cm. diameter) and also drilled from one edge to the centre. These holes are well lined with pitch, and plates of glass are then cemented with pitch to the sides of the block. The cylin-

dricul trough is filled through the narrow hole, which is then closed by a paraffined cork. The troughs can be used for acid solutions, but not for alcohol or benzene. T. M. L.

**Formation of Negative Images by the Action of Certain Vapours.** By P. VIGNON (*Compt. rend.*, 1902, 134, 902—904).—It has been shown by Colson (*Abstr.*, 1896, ii, 601) that vapours emitted from zinc are capable of acting on a photographic plate. The author has obtained images of medals, &c., powdered over with zinc dust, by mere contact with the photographic plate. Although such images are not perfectly sharp, presenting the appearance of being viewed through a gauze screen, yet they are vigorous. Negatives have also been obtained by the action of ammoniacal vapours on linen treated with a mixture of powdered aloes and olive oil. A gloved plaster hand moistened with ammonium carbonate leaves, on this account, a photographic imprint on such linen. L. M. J.

**The New Gas from Radium.** By E. RUTHERFORD and Miss H. T. BROOKS (*Chem. News*, 1902, 85, 196—197; from *Trans. Roy. Soc. Canada*, 1902, [ii], 7, 21).—The rate of diffusion of the emanation from a radium preparation was determined by an electrical method similar to that employed by Loschmidt (*Wiener Akad.*, 1871) in his experiments on the interdiffusion of gases. The emanating power of radium is increased 10,000 times by heating it to below a red heat, but is destroyed to a large extent by heating to a higher temperature. The values found for the coefficient of diffusion of the emanation into air lie between 0.08 and 0.15. As this coefficient varies inversely with the molecular weight, it is concluded that the emanation is not radium vapour, but a radioactive vapour or gas with a molecular weight between 40 and 100. It is probable that the emanation from thorium is of a similar character. J. McC.

**Absorption of Radioactivity by Liquids.** By THOMAS TOMMASINA (*Compt. rend.*, 1902, 134, 900—902).—The author has obtained results similar to those obtained by Curie regarding the absorption of radioactive radiation by liquids and the consequent conductivity of dielectrics (this vol., ii, 298). The apparatus employed is described, and a table given of qualitative results on the absorption by a number of liquids comprising both organic compounds and aqueous solutions. L. M. J.

**The Radioactive Elements considered as Examples of Elements undergoing Decomposition at the Ordinary Temperature, together with a Discussion of their Relationship to the other Elements.** By GEOFFREY MARTIN (*Chem. News*, 1902, 85, 205—206).—The author argues that as an element is heated it casts off electrons, and when this occurs the element is radioactive. According to his views, there exists for every element a temperature range at which this takes place, and he consequently regards radioactivity as a general property of matter. In the case of the ordinary radioactive substances, the ordinary temperature falls within the particular temperature range. The paper is purely speculative. J. McC.

**Electrical Resistance of Steel and Pure Iron.** By CARL BENEDICKS (*Zeit. physikal. Chem.*, 1902, 40, 545—560).—Equivalent quantities of carbon, chromium, and other elements dissolved in steel cause an equal increase of hardness and determinations of the resistance of a number of samples of steel containing silicon, sulphur, phosphorus, and manganese indicated that the resistance is also equally affected by equivalent quantities of these elements, and may be calculated by the expression  $S = 7.6 + 26.8 \Sigma C$ , where  $S$  is the resistance in microhms per c.c., and  $\Sigma C$  is the percentage of foreign substances calculated as equivalent quantities of carbon. The dissolved carbon alone is of influence, the precipitated carbon having no effect, but the experiments indicate that pure steel always contains about 0.27 per cent. of dissolved carbon, a result in accord with many metallurgical analyses. The resistance of perfectly pure iron is hence 7.6 microhms per c.c.; this value is less than any directly determined, but absolutely pure iron has never been investigated (see Abstr., 1901, ii, 374).

L. M. J.

**Improvement of Apparatus employed for the Measurement of the Dielectric Constant.** By PAUL DRUDE (*Zeit. physikal. Chem.*, 1902, 40, 635—637).—An improvement on the apparatus previously employed by the author (Abstr., 1897, ii, 438).

L. M. J.

**Some Phenomena of Voltaic Polarisation.** By MARCELLIN BERTHELOT (*Compt. rend.*, 1902, 134, 865—873).—In the simple voltaic cells investigated by the author (this vol., ii, 375, 376), it is shown that the addition of hydrogen or a reducing agent to the liquid at the negative electrode develops an *E.M.F.* of opposite sign and hence causes polarisation. Thus, in a cell containing solutions of sodium chloride at different concentrations, the *E.M.F.* fell from 0.12 volt to 0.026 volt when placed in an atmosphere of hydrogen, and again rose to the normal value when the hydrogen was replaced by nitrogen. Similar results were obtained with cells of lactic acid and sodium hydrogen carbonate. In an element of a Grove's battery, the electrodes are gaseous hydrogen and oxygen, and the *E.M.F.* is about 1.05 volts, although the decomposition of water necessitates between 1.5 and 1.6 volts. This the author considers to be due to the formation of platinum hydrides, the heat of formation of which, although variable for different states of the platinum, would be equivalent to about 0.6 volt. Experiments are also described on the polarisation effects of the addition of hydrogen peroxide and of pyrogallol to the different electrode liquids.

L. M. J.

**Electro-chemical Studies with Acetylene. I. Cathodic Depolarisation.** By JEAN BILLITZER (*Monatsh.*, 1902, 23, 199—216).—In alkaline or acid solution, acetylene acts as a depolariser towards a platinised cathode. When a current is passed between platinised electrodes in a voltameter containing aqueous acid or alkali through which acetylene is bubbled and the potential of the cathode measured against a free hydrogen electrode in the same acid or alkaline solution, it is found that ethylene, and afterwards ethane,



are given off before the potential of the cathode has fallen to that of the hydrogen electrode. With a higher *E.M.F.*, hydrogen is added to the products.

With platinum electrodes, the presence of acetylene, nitrogen, or carbon dioxide results in a rise in the *E.M.F.* required for the liberation of hydrogen. Electrolysis of acetylene in normal sulphuric acid solution with a mercury cathode leads to the formation of traces of alcohol. G. Y.

**Electromotive Force of Metals in Solutions of Cyanide.** By S. B. CHRISTY (*Amer. Chem. J.*, 1902, 27, 354—420. Compare this vol., ii, 193).—The *E.M.F.* of potassium cyanide against silver decreases from +0.34 volt for *M* solutions to -0.5 volt for *M*/1,000,000 solutions. Similarly, for zinc, the values decrease from +0.945 to +0.330 volt; for lead from +2 to +0.04 volt; for mercury from +0.15 to -0.635 volt; in the case of iron, the values increase from -0.03 to -0.16 volt (*M* = gram-molecule per litre).

The solubility of gold in solutions of potassium cyanide of different strengths was determined; for all practical purposes, the cyanide ceases to act at a dilution below 0.001 per cent. E. G.

**Researches on Electromotive Force.** By MARCELLIN BERTHELOT (*Compt. rend.*, 1902, 15, 793—807).—The author first considers at some length the various causes of difference between the actual thermal value of a chemical reaction, the apparent value under the conditions of the voltaic cell, and the voltaic thermal value. Determinations were then made of the *E.M.F.* produced by simple liquid mixtures in which there is no action of the liquid on the electrode. The following cases were investigated: (1) Action of an acid on a base. (2) Action of an acid on its sodium or ammonium salt. (3) Action of an alkaline base on a salt of the same base. (4) Action of acids on salts of other acids. (5) Action between two solutions of the same salt at different concentrations. In the first case, electromotive forces of about 0.5 volt were obtained, the values being lower than those calculated from the heats of neutralisation. In all the other sets of experiments, values varying from 0.1 to 0.4 volt were obtained, but in no case could exterior electrolysis be produced by the use of a number of cells. L. M. J.

**Temperature Variations of the Specific Molecular Conductivity and of the Fluidity of Sodium Chloride Solutions.** By THOMAS R. LYLE and RICHARD HOSKING (*Phil. Mag.*, 1902, [vi], 3, 487—498. Compare Hosking, *Abstr.*, 1900, ii, 336).—The ratio of the specific molecular conductivity to the fluidity for a given concentration decreases proportionally to rise of temperature, and the temperature coefficient involved is the same for all concentrations. It is noted that for the stronger solutions at least the degree of dissociation decreases markedly with rise of temperature. J. C. P.

**Method for Establishing the Electrolytic Action of a Pile.** By MARCELLIN BERTHELOT (*Compt. rend.*, 1902, 134, 873—876).—The author describes the method by which electrolytic action is detected,

and the apparatus employed for the purpose. The cells used were a Daniel of *E.M.F.* 1.06 volts, a zinc-cadmium cell of *E.M.F.* 0.35 volt, and a zinc-platinum cell of *E.M.F.* 0.80 volt. The *E.M.F.* required for the decomposition of water was found to be between 1.50 and 1.60 volts, and if pyrogallol or formaldehyde be added, between 0.70 and 0.80 volt.

L. M. J.

**Disintegration and Pulverisation of Cathodes due to the Formation of Alloys with Alkali Metals.** By FRITZ HABER and M. SACK (*Zeit. Elektrochem.*, 1902, 8, 245—255).—The disintegration and pulverisation of cathodes in alkaline solutions were observed by Bredig and Haber (*Abstr.*, 1898, ii, 78) and ascribed to the formation of alloys with alkali metals. The subject is now more fully investigated by observing the polarisation at lead and tin cathodes, and by measuring the potential difference between alkali metal alloys and a solution of lithium chloride (1.56 per cent.) in methyl alcohol, cooled by a mixture of solid carbon dioxide and ether. All the *P.D.*'s given are referred to an anode of mercury in contact with mercurous oxide and a normal solution of sodium hydroxide.

With a lead cathode in a solution of sodium hydroxide, pulverisation of the cathode began at 2.4 to 2.5 volts, a *P.D.* slightly lower than that between sodium and the lithium chloride solution, 2.7 volts. (The latter is not very different from the *P.D.* between sodium and a solution of sodium hydroxide at the ordinary temperature). At a lower *P.D.* (1.7 volts), hydrogen begins to be evolved, and the surface of the cathode is more or less disintegrated.

Alloys of sodium and lead containing 4.5 per cent. of sodium are brittle, act very slowly on water, and exhibit the same *P.D.* as lead (0.6 volt); those with 8 per cent. of sodium and more give a sudden pulverisation with water. The *P.D.* increases from 1.8 volts at 8 per cent., to about 2 volts with 30 per cent. of sodium. The pulverisation of the weaker alloys is only observed for a moment when a fresh surface comes into contact with water, whereas the more concentrated sodium alloys are pulverised completely and rapidly.

Tin behaves in the same way as lead; hydrogen is first evolved at 1.3 to 1.4 volts, and the metallic surface is etched; pulverisation begins at 2.3—2.4 volts. Alloys containing 8.6 per cent. of sodium show indications of pulverisation. Those with less than 6 per cent. do not. The *P.D.* between alloy and cooled lithium chloride solution shows a sudden increase from about 0.3 volt to about 1.4 volts at this point.

Zinc is neither disintegrated nor pulverised. The authors also failed to prepare alloys of sodium with it.

Platinum, heated to redness with sodium and then placed in alcohol, lost several decigrams of grey powdered platinum.

The *P.D.* between frozen sodium amalgams and the lithium chloride solution is about 0.7 volt less than the value found for sodium for all amalgams containing more sodium than corresponds with the formula  $\text{Hg}_5\text{Na}$ . Those containing less sodium have the same *P.D.* as mercury. The authors conclude that the dilute amalgams consist of a solution of  $\text{Hg}_5\text{Na}$  in mercury. The measurements throw no light on the composition of those containing more sodium.

T. E.

**Reducing Action of Lead and Mercury Cathodes in Solutions containing Sulphuric Acid.** By JULIUS TAFEL and KARL SCHMITZ (*Zeit. Elektrochem.*, 1902, 8, 281—288).—The experiments described previously (Abstr., 1900, ii, 588) are completed by careful comparative experiments on the relative efficiency of mercury and lead cathodes in the reduction of caffeine, which show that the mercury cathode is the better, the current efficiency being about 84 per cent., whilst with lead it is about 52 per cent. The addition of small quantities of tin to the mercury reduces its efficiency very rapidly.

In an alcoholic solution of sulphuric acid, at a mercury cathode, camphor is reduced to borneol, whereas at a lead cathode practically no reduction occurs.

Acetone is very slowly reduced at a lead cathode, the main product being pinacone. Under the same circumstances, the reduction at a mercury cathode takes place much more rapidly and also goes further, the acetone being converted quantitatively into isopropyl alcohol.

T. E.

**Behaviour of Platinum and Platinum-Iridium Anodes in the Electrolysis of Hydrochloric Acid.** By FR. BRAN (*Zeit. Elektrochem.*, 1902, 8, 197—201).—Haber and Grinberg have shown that platinum anodes are attacked more readily in concentrated than in dilute hydrochloric acid. The author now finds that in an acid of given strength the attack diminishes as the current density increases. This is explained by the diminution of the concentration of the acid in contact with the anode which is produced by the current, the diminution being greater with high current density. Platinum-iridium is less attacked than platinum.

T. E.

**Formation of Insoluble Precipitates by Means of Electrolysis with Soluble Anodes.** By MAX LE BLANC and EMIL BINDSCHEDLER (*Zeit. Elektrochem.*, 1902, 8, 255—264).—The formation of lead chromate by the electrolysis of a solution of sodium chlorate and chromate with a lead anode is investigated. With solutions containing from  $1\frac{1}{2}$  to 12 per cent. of salt, 70 to 90 per cent. of which is chlorate, the lead chromate is formed near the anode, separating from it by its own weight, whereas in solutions containing a large proportion of chromate an adherent layer of chromate and peroxide of lead forms on the anode. The yield of lead chromate is theoretical in the first case, practically zero in the latter. Sodium nitrate, acetate, or butyrate give practically the same result as chlorate. With the mixed electrolyte, the current is mainly transported by  $\text{ClO}_2$  ions, the chromate ions are therefore soon removed almost completely from the electrolyte in contact with the anode, and the precipitation of lead chromate takes place at some small distance from it. With a more concentrated chromate solution, this is not the case.

T. E.

**Theory of the Direct Method of Determining Ionic Velocities.**—By RICHARD ABEGG and W. GAUS (*Zeit. physikal. Chem.*, 1902, 40, 737—745).—The paper deals with some points raised by Steele's work (Trans., 1901, 79, 414, and this vol., ii, 241).—The influence of the initial concentrations of the neighbouring electrolytes has been

studied, and it is recommended that in Steele's method the concentration in the indicator jelly should be at least equivalent to that in the middle electrolyte. The differences between the results obtained by Hittorf's method and those obtained by Steele's direct method are attributed to the influence of cataphoresis on the moving boundaries. When a correction for this influence is applied, Steele's method gives the same value for the transport number of chlorine as Hittorf's method.

The authors recommend a different method of illuminating the moving boundaries. J. C. P.

**Determination of the Freezing Point Depression Constant for Electrolytes.** By THOMAS C. HEBB (*Trans. Nov. Scot. Inst. Sci.*, 1902, 10, 409—421).—The expression  $\delta = k(1 - \alpha) + l\alpha$  is employed to obtain the depression constant,  $\alpha$  being the ionisation coefficient and  $k$  and  $l$  being constants. If  $\delta$  is therefore plotted against  $\alpha$ , a straight line should be obtained, and the author, after mapping these curves resulting from the work of different observers, has calculated the values of  $k$  and  $l$  from the portions of the curves which approximate most closely to straight lines. From these, the depression constants for undissociated molecules and free ions are obtained for potassium, sodium, hydrogen, barium, and ammonium chlorides; potassium and hydrogen nitrates; potassium hydroxide; potassium, sodium, hydrogen, and magnesium sulphates, and orthophosphoric acid. The constants for the ions do not vary greatly, and in all cases are not far removed from the theoretical value. The constants for the undissociated molecules, however, differ greatly, varying from 0.8—2.8, a result the author considers due to the fact that this constant cannot be determined as accurately as the former. The mean values obtained are respectively 1.851 and 1.932. L. M. J.

**Liquid Mixtures of Minimum Boiling Point.** By CLIFFORD D. HOLLEY (*J. Amer. Chem. Soc.*, 1902, 24, 448—457).—By the boiling point process, the following minima have been found: 12.7 parts of amyl alcohol (b. p. 129°) and 87.3 parts of amyl bromide (b. p. 117.9°) give a liquid with boiling point 116.15°; 63.6 parts of isobutyl alcohol (105°) and 36.4 parts of amyl bromide (118.1°) give a liquid with boiling point 103.4°, the minimum point, however, is not very sharply marked; 70.7 parts of propyl alcohol (95.5°) and 29.3 parts of amyl bromide (118.2°) give a liquid with boiling point 94° (propyl alcohol may contain up to 65 per cent. of amyl bromide without having its boiling point raised); a mixture of 52 parts of amyl alcohol (128.9°) and 48 parts of amyl iodide (146.5°) boils at 127.3°; with mixtures of isobutyl alcohol or propyl alcohol with amyl iodide, no definite minimum could be found; 97.4 parts of amyl alcohol and 2.6 parts of amyl acetate give a mixture which boils at 129.1° (lower by 0.2° than the boiling point of the original alcohol). The following mixtures show no minimum boiling point: amyl alcohol with ethyl butyrate or bromoform; amyl acetate with ethylene bromide, amyl bromide, amyl iodide, bromoform or ethyl butyrate; and amyl bromide with ethyl butyrate or toluene. J. McC.

**An Extension of the Idea of the Critical Constants.** By ALEXIUS BATSHINSKI (*Zeit. physikal. Chem.*, 1902, 40, 629—634).—The terms orthomeric and allomeric are suggested for compounds in which the molecular state is respectively (1) the same, and (2) different, in the liquid and saturated vapour. In a polymerised compound, the critical constants cannot be calculated by the law of corresponding states, and the values obtained by such a calculation, in the case of an orthomeric compound, are termed the meta-critical values, which vary with the temperature for which the calculation is made. The values of these meta-critical constants may, however, be used to determine the state of aggregation. Thus, for the critical constants  $p_1 v_1 M / T_1 = 16170$ , for the meta-critical constants  $PV\alpha M / T = 16170$ , where  $\alpha$  is the aggregation coefficient. The values thus obtained for acetic acid at 100°, 200°, and 300° agree satisfactorily with those obtained by Ramsay and Shields. L. M. J.

**Measurements of Critical Constants. III.** By PHILLIPE A. GUYE and ED. MALLET (*Arch. Sci. phys. nat.*, 1902, [iv], 13, 462—489).—The concluding paper of a series (this vol., ii, 242, 302), in which the results are discussed. The conclusions arrived at have appeared previously (this vol., ii, 195, 243). L. M. J.

**Determination of Inversion Temperature of Kelvin Effect in Hydrogen.** By KARL OLSZEWSKI (*Phil. Mag.*, 1902, [vi], 3, 535—540).—Pure hydrogen under high pressure is cooled by passing through a worm tube immersed in a suitable bath, and then allowed to escape into a box packed with chamois leather, expanding at the same time to atmospheric pressure. The box contains a resistance thermometer, which indicates whether the process of expansion is accompanied by a heating or a cooling effect. It has been found that above  $-80.5^\circ$  the expansion is accompanied by a heating, below  $-80.5^\circ$  by a cooling, effect; that temperature, therefore, is the temperature of inversion of the Kelvin effect for hydrogen. J. C. P.

**Volume Relations and Optical Characters of Isomorphous Mixtures.** By GEORG WULFF (*Zeit. Kryst. Min.*, 1902, 36, 1—14).—Retgers has shown that the sp. gr. (or sp. volume) of isomorphous mixtures is proportional to the chemical composition. It is now demonstrated, from determinations of the angles of optical extinction, that the refractive indices of mixed crystals of the series  $R'_2 M''(SO_4)_2 \cdot 6H_2O$  are proportional to their volumes. L. J. S.

**Significance of Changes of Atomic Volume II. Probable Source of Heat of Chemical Combination and a New Atomic Hypothesis.** By THEODORE W. RICHARDS (*Zeit. physikal. Chem.*, 1902, 40, 597—610).—The decrease of molecular volume in the formation of a number of metallic chlorides is compared with the heat of formation, and it is seen that there is an approximate parallelism between them; this is clearly evident when the values are recorded on the same diagram. A similar connection obtains in the case of metallic bromides and in the haloids of potassium. The author hence considers

it probable that the work necessary for the contraction resulting in the formation of a solid or liquid compound from two other elements or compounds is approximately proportional to the heat developed. It is stated that the work actually necessary for the compression of the equivalent quantities of sodium and chlorine into sodium chloride is actually of the same order of magnitude as the heat developed, but the values are not given. The author suggests an explanation, the fundamental basis of which is the supposition that the atoms themselves are elastic and compressible.

L. M. J.

**Osmotic Pressure of some Solutions Calculated from the E.M.F. of Concentration Elements.** By T. GODLEWSKI (*Bull. Acad. Sci. Cracow*, 1902, 146—163).—The *E.M.F.* of the elements,  $\text{Hg} | \text{HgCl} | \text{ZnCl}_2 | \text{Zn}$  (amalgam);  $\text{Hg} | \text{Hg}_2\text{SO}_4 | \text{CdSO}_4 | \text{Cd}$  (amalgam); and  $\text{Hg} | \text{HgCl} | \text{CdCl}_2 | \text{Cd}$  (amalgam), with varying concentration of zinc chloride, cadmium sulphate, and cadmium chloride respectively, was determined. The variation of the *E.M.F.* with the logarithm of the ratio ( $f$ ) of the concentration is given diagrammatically; at low concentrations, the *E.M.F.* increases slowly with  $\log h$ , but afterwards more quickly. The variation of the value of  $f/h$  with  $h$ , where  $f = (hiRTw)/m$ ,  $w$  being the specific volume of the solvent and  $m$  the molecular weight of the dissolved substance, has been traced. The value of  $f/h$  has a minimum value when the solution contains 0.73 gram-mol. of zinc chloride, 0.15 gram-mol. of cadmium sulphate, or 0.4 gram-mol. of cadmium chloride; this is not contradictory to the theory of electrolytic dissociation, but it shows that the gas laws can only be applied to solutions considerably more dilute than those corresponding with the minimum points. From the results obtained, the osmotic pressure and the degree of dissociation have been calculated with the aid of the theoretical considerations of Duhem and of Natanson, account being taken of the compressibility of water. The results are not in very good agreement with those obtained from the depression of the freezing point, the raising of the boiling point, or the conductivity.

J. McC.

**Retrograde Diffusion of Electrolytes.** By J. THEVERT (*Compt. rend.*, 1902, 134, 826—827).—If a solution containing an acid and another electrolyte be placed in communication with an equally concentrated solution of this electrolyte, not only does the acid diffuse, but also the electrolyte, so that during the first stages of the experiment its concentration, originally uniform, may vary considerably in different places. Thus, in one of the recorded experiments, hydrogen chloride was allowed to diffuse into a solution of sodium chloride of concentration 0.39. After 47 hours, the concentration of the sodium chloride was found to be, upper part, 0.373; middle, 0.380; lower, 0.405. These results are in accord with the electrolytic theory of diffusion.

L. M. J.

**So-called Liquid Crystals. II.** By GUSTAV TAMMANN (*Ann. Physik.*, 1902, [iv], 8, 103—108. Compare Abstr., 1901, ii, 231).—The author brings forward further evidence in support of his contention

that the so-called liquid crystals are merely emulsions. Separation of the liquids causing the emulsion can be effected, and it appears that *p*-azoxyphenetole, as usually prepared, is not chemically homogeneous. If *p*-azoxyanisole is sealed up in a tube hung vertically in an oil-bath and the temperature is slowly raised from its melting point, the turbidity of the uppermost layers disappears at  $119.7^{\circ}$ , and the clearing gradually extends to the lower layers, being complete at  $135^{\circ}$ . If the tube is allowed to cool, the same changes are observed in the reverse order; the lowest layers become turbid first, and the turbidity extends upwards, the uppermost layers becoming turbid at  $119^{\circ}$ . If the contents of the tube are stirred while the temperature is rising, turbidity disappears throughout the tube at  $134.5^{\circ}$ . This dependence of the temperature of clearing on the depth below the surface is characteristic of emulsions. J. C. P.

**Decomposition of Hydrated Mixed Crystals.** By REINHARD HOLLMANN (*Zeit. physikal. Chem.*, 1902, 40, 561—576).—An investigation into the phenomena of decomposition and formation of hydrated mixed crystals in solution. Three types of curve are obtainable, in which the decomposition temperature for any mixture (1) lies between those of the components, (2) reaches a maximum value, (3) has a minimum value. It is shown in the first type of mixture that at any determined temperature the mixed crystals of a higher hydrate are, in comparison with those of a lower hydrate, always richer in that component the addition of which raises the decomposition temperature. Mixtures of the heptahydrates of zinc and manganese sulphates were examined, the series being an example of the first of the above types. L. M. J.

**Double Salts of Zinc and Magnesium Sulphates.** By REINHARD HOLLMANN (*Zeit. physikal. Chem.*, 1902, 40, 577—580).—It has been previously shown by the author that in the case of mixed crystals of the heptahydrates of zinc and magnesium sulphates, two compounds exist in which the ratios of magnesium to zinc are respectively 2 : 1 and 1 : 1 (*Abstr.*, 1901, ii, 436). This is verified by the curve for the decomposition temperature, which is made up of three distinct curves with points of intersection where the ratios of magnesium to zinc are as just mentioned. Of these three curves, the first, from  $\text{MgSO}_4$  to  $2\text{MgSO}_4, \text{ZnSO}_4$ , is of the first type described in the preceding abstract, the other two curves are of the second type, the maximum decomposition temperatures agreeing with the points of minimum vapour pressure (*loc. cit.*). L. M. J.

**Composition of Hydrates of Gases.** By ROBERT DE FORCRAND (*Compt. rend.*, 1902, 134, 835—838).—The experimental determination of the composition of the hydrate of a gas is a matter of considerable difficulty, and for many such hydrates very diverse results have been obtained by different observers. The relation  $Q/T = 30$  may be applied in such cases to determine the number of mols. of water in the hydrate. In this expression,  $Q$  is the heat of formation from *solid* water, whilst  $Q_1$ , the heat of formation from liquid water, may be experimentally determined or deduced from the pressure curve by Clapeyron's formula.

The difference  $Q - Q_1$  is hence the heat of solidification of the water of the hydrate, and the number of mols. of water is therefore known.

L. M. J.

**Reciprocal Nature of Solubility Influences.** By VICTOR ROTHMUND and N. T. M. WILSMORE (*Zeit. physikal. Chem.*, 1902, 40, 611—628).—It is deduced theoretically that if the solubility of a compound  $A$  is lowered by the addition of  $B$ , then also the solubility of  $B$  is lowered by the addition of  $A$ . The quantitative connection is investigated, and the relation obtained is  $l_1 \log (L_1/l_1) = l_2 \log (L_2/l_2)$ , where  $L_1$  and  $L_2$  are the solubilities of the pure compounds, and  $l_1$ ,  $l_2$  the solubilities in a saturated solution of both. In the case of a non-electrolyte and dissociable compound, the first expression becomes  $il_1 \log (L_1/l_1)$ . As the partition coefficient gives the ratio of the solubilities in the two solvents, the ratio  $L_1/l_1 = K/k$ , where  $K$  and  $k$  are the partition coefficients with an indifferent solvent. The validity of the expression was verified by experiments on the solubility of salts in aqueous phenol and acetic acid, and on the effect of salts on the partition of these two compounds between water and chloroform.

L. M. J.

**Mechanism of the Catalytic Action of Iodine on the Bromination of Benzene.** By LUDWIK BRUNER (*Bull. Acad. Sci. Cracow*, 1902, 181—200. Compare Abstr., 1901, ii, 441).—The results of an investigation of the action of bromine on benzene in presence of iodine give a constant for  $K = 1/t \cdot \log x/(A - x)A$ , where  $t$  is the time,  $A$  the initial concentration of the bromine, and  $x$  the quantity which has reacted. This would indicate that the reaction is bimolecular. The reaction has been followed in solutions so dilute that there was only 1 gram-mol. of bromine to 25 gram-mols. of benzene, and a constant value has throughout been obtained for  $K$ . The extent of bromination depends on the concentration of the iodine, and it appears that reaction either ceases or becomes excessively slow when the residual bromine and the iodine are present in equivalent proportions.

Using Ostwald's method of determining the order of the reaction (quantity of substance transformed is inversely proportional to the velocity factors), it is found that the bromination of benzene in presence of iodine is a quadrimolecular reaction and takes place according to the equation:  $C_6H_6 + 4Br = C_6H_5Br + HBr_3 = C_6H_5Br + HBr \rightleftharpoons Br_2$ . Since the amount of bromine united with the hydrogen bromide is double that which has entered into reaction with the benzene, the reaction must appear of a lower order when this is calculated by van't Hoff's method. The bromination is carried out by free atoms of bromine and not by this substance in the molecular condition. The cause of the greater velocity in presence of iodine is that iodine bromide dissociates ( $IBr \rightleftharpoons I + Br$ ) more easily than bromine ( $Br_2 \rightleftharpoons 2Br$ ). The author discusses the rôle of dissociation in chemical reactions in general.

J. McC.

**Antiseptic Function of the Hydrogen Ions of Dilute Acids.** By MANFRED BIAL (*Zeit. physikal. Chem.*, 1902, 40, 513—534).—From the antiseptic effect of various salts and acids on certain spores, Paul



and Krönig concluded that this antiseptic action was not proportional to the concentration of the hydrogen ions, although such proportionality existed for certain weak acids (Abstr., 1897, ii, 155). The author has determined the effect of dilute acids in inhibiting yeast fermentation and compared the action of different acids on the same culture. The acids employed were hydrochloric, sulphuric, phosphoric, acetic, oxalic, formic, propionic, and butyric acids. The acids may be roughly divided into three groups, which are also equal dissociation groups, and the author considers that the antiseptic action is proportional to concentration of the hydrogen ions. The addition of a normal salt with similar cation caused a great decrease of the effect; by further addition, a minimum is reached after which the antiseptic action increases owing to the effect of the salt itself, this being completely analogous to the action of normal salts on inversion velocity.

L. M. J.

**Distinction between Polymorphism and Chemical Isomerism.**  
By GIUSEPPE BRUNI (*Atti R. Accad. Lincei*, 1902, [v], 11, i, 386—389). —The author discusses Wegscheider's paper (Abstr., this vol., ii, 126) on this question. The distinction between isomerism and polymorphism is that although each of two isomerides has a stable melting point in the sense of the phase theory, this is only the case with one of two polymorphs, the melting point of the other corresponding with a condition of unstable equilibrium which is destroyed by the presence of the smallest trace of the other form. Wegscheider's criterion for the existence of isomerism (that the form which is more stable in the neighbourhood of the melting point will have the lower melting point) is perfectly correct, but the conception of greater or less stability involved in it is more vague than, and quite different from, that of the stability or instability of a solid phase in equilibrium with a liquid phase. The true criterion for polymorphism or isomerism is this: If two compounds are isomerides, the addition of one of them to the other causes a change exactly similar to that brought about by the addition of any other compound, that is, the melting point is lowered and we have the well-known system of two descending curves meeting in a cryohydrate point at which the two forms of crystals co-exist. When one of the isomerides undergoes rapid transformation into the other form, it will be difficult or impossible to trace quantitatively the curve of fusion, but it will be possible to realise and to observe points of fusion either intermediate to those of the two isomerides or lower than either of them. With polymorphs, however, a quite different behaviour is observed. The melting point of the stable form is scarcely altered by the addition of the unstable modification, whilst the melting point of the latter is changed to that of the other form when the last is added in any proportion whatever. If, however, every trace of crystalline matter be destroyed by heating and the mixture be slowly cooled, the solidification point of the labile form may be realised. With polymorphs, these two solidification points are the only two obtainable; intermediate or inferior points, as well as a cryohydric point at which both kinds of crystals can exist, are here impossible.

T. H. P.

**Calculation of Atomic Weights.** By FRANK W. CLARKE (*Amer. Chem. J.*, 1902, 27, 321—328).—Attention is called to the desirability of distributing the errors of observation in the calculation of atomic weights instead of concentrating them on a single factor. Examples are given in which, by combining a number of ratios and assigning to each measurement weight inversely proportional to the square of its probable error, the influence of experimental error is divided up and distributed and even the influence of systematic error is diminished.

E. G.

**Atomic Weight Numbers.** By ALOIS BILECKI (*Chem. Zeit.*, 1902, 26, 399).—Attention is drawn to the fact that if the atomic weight of oxygen is taken as unity, a series of numerical relations between atomic weights of other elements become apparent.

K. J. P. O.

**The Nature of Radicles.** By FERDINAND HENRICH (*Ber.*, 1902, 35, 1773).—A *résumé* of the history of the theory of radicles not suitable for abstraction (compare *Abstr.*, 1899, i, 469, 794; 1900, i, 429; *Vorländer*, *Abstr.*, 1899, i, 312, 309; ii, 250).

G. T. M.

**Chemical Method for obtaining Vacua.** By FRANCIS G. BENEDICT and CHARLOTTE R. MANNING (*Amer. Chem. J.*, 1902, 27, 340—345).—The upper compartment of a Hempel desiccator is provided with fresh, dry sulphuric acid. After the material to be dried has been introduced, 10 c.c. of dry ether are poured on the floor of the desiccator and the cover is replaced. The pressure is now reduced by means of the water-pump to 60—40 mm. The stop-cock is closed and, owing to the absorption of the ether vapour by the sulphuric acid, in 8—10 minutes a vacuum of 4—1 mm. is obtained.

E. G.

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## Inorganic Chemistry.

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**Potential of Ozone.** By LEOPOLD GRÄFENBERG (*Zeit. Elektrochem.* 1902, 8, 297—301).—The *E.M.F.* of the hydrogen-ozone gas cell is found to be 1.65 volts for 10 per cent. ozone, or 1.66 volts for pure ozone. This value is very near the discharge potential of hydroxyl ions and it is pointed out that it is probable that ozone is formed by the reversible reaction,  $6\text{OH}' \rightleftharpoons \text{O}_3 + 3\text{H}_2\text{O}$ . T. E.

**Generator for Hydrogen Sulphide.** By J. N. SWAN (*J. Amer. Chem. Soc.*, 1902, 24, 476—477).—The apparatus consists of two two-necked Woulff bottles. One of these having a side tube at the bottom contains iron sulphide and acid is introduced by means of a dropping funnel. The gas then passes into the other bottle, which serves the double purpose of washing it and collecting it over water. The dis-

placed water is forced up into a tube fitted with a large bulb. By opening the stop-cock fitted to an exit tube the gas becomes available for use.

L. DE K.

**Theory of the Lead Chamber Process.** By FR. RIEDEL (*Zeit. angew. Chem.*, 1902, 15, 462—465).—An attempt has recently been made by Meyer (*Zeit. angew. Chem.*, 1901, 14, 1245) to apply the law of mass action to the formation of sulphuric acid in the lead chamber. Lunge (*Zeit. angew. Chem.*, 1902, 15, 147) has criticised this adversely and the author now adversely criticises Lunge's statement. The author believes that the law of mass action can be applied to the process, but only approximate results can be obtained, because the temperature and the concentrations vary at different points in the chamber. He further points out that chemical dynamics is not sufficiently developed to indicate the temperature optimum for any reaction, although Lunge has attempted to decide this for the particular reaction in question.

J. McC.

**Electrolytic Preparation of Persulphates without a Diaphragm.** By ERICH MÜLLER and O. FRIEDBERGER (*Zeit. Elektrochem.*, 1902, 8, 230—236).—A saturated solution of potassium hydrogen sulphate is electrolysed at a low temperature (7°) without a diaphragm. Platinum electrodes are used and the current density at the anode is about 0.5 ampere per sq. cm. The yield of potassium persulphate is 35 per cent. of the theoretical quantity.

By using a saturated solution of ammonium sulphate containing a small quantity of potassium dichromate (1 gram to 500 c.c. of solution), 80 per cent. of the theoretical yield of ammonium persulphate is obtained, provided that the ammonia formed is neutralised from time to time with sulphuric acid.

T. E.

**Synthesis of Ammonia by Electricity.** By ALEXANDER DE HEMPTINNE (*Bull. Acad. roy. Belg.*, 1902, 28—35).—When a mixture of nitrogen and hydrogen in the proportion 1 : 3 is subjected to electric discharges, the amount of ammonia formed is influenced by the temperature and pressure of the gas mixture and by the mode of application of the discharge. The rate of combination increases as the sparking distance is diminished and a similar effect is produced by lowering of temperature or diminution of pressure. Pressure exerts less influence when sparks derived from a Tesla coil are used or when the discharge is silent than is the case when a Ruhmkorff coil is employed. Control experiments showed that combination is effected, not by the glowing platinum of the terminals, but by the electric discharge itself.

T. A. H.

**Method of Preparation of Azoimide.** By SIMEON M. TANATAR (*Ber.*, 1902, 35, 1810—1811. Compare Abstr., 1899, ii, 479).—On oxidising a mixture of hydrazine and hydroxylamine in mol. proportion in acid solution by means of bromine water, permanganic acid, lead dioxide, or red lead, a small quantity of azoimide is always formed. When hydrogen peroxide is used, a yield of 24.3 per cent. is obtained,

and with chromic acid, a yield of 29.27 per cent. In both cases, the oxidising agent is slowly added to a hot solution of the two bases in dilute sulphuric acid; the azoimide is then distilled off.

K. J. P. O.

**Oxidation of Nitrite by Permanganate.** By JOHN WADDELL (*Chem. News*, 1902, 85, 158).—By treating sodium nitrite with a small quantity of a mixture containing the desired proportion of permanganate and sulphuric acid, then warming slightly with a few drops of sulphuric acid, adding the remainder of the mixture and completing the reaction by the addition of a few drops or so of permanganate, a slightly cloudy neutral solution is produced and the reaction nearly corresponds with that represented by the equation:  $5\text{NaNO}_2 + 3\text{H}_2\text{SO}_4 + 2\text{KMnO}_4 = 5\text{NaNO}_3 + \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O}$ , in which an excess of sulphuric acid is not necessary.

D. A. L.

**Acids of Phosphorus. II. Velocity of Hydration of Pyrophosphoric Acid.** By CLEMENTE MONTEMARTINI and U. EGIDI (*Gazzetta*, 1902, 32, i, 381—388. Compare Abstr., 1901, ii, 551).—The authors have measured the velocity of transformation of pyrophosphoric into orthophosphoric acid at a temperature of 19° and in solutions of different concentrations. The reaction, which proceeds according to the equation  $\text{H}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O} = 2\text{H}_3\text{PO}_4$ , was controlled acidimetrically. The results show that metaphosphoric acid undergoes hydration much more slowly than pyrophosphoric acid, which cannot be kept unchanged for very long even when in dilute solution. For low concentrations of pyrophosphoric acid the hydration is but little influenced by the catalytic action of the hydrogen ions, which, however, exert a considerable effect in the more concentrated solutions. It is pointed out that, unlike the acids themselves, salts of metaphosphoric and pyrophosphoric acids are very stable in solution, and undergo hydration with difficulty.

T. H. P.

**Fusion of Carbon.** By A. LUDWIG (*Zeit. Elektrochem.*, 1902, 8, 273—281).—The experiments were made in a vessel filled with hydrogen under a pressure of 1500 to 3000 atmospheres. Carbon rods, with their ends in contact with each other, were heated by an electric current; after a few seconds, the current sank to nothing, soon increasing again to its former strength. This went on for some minutes. The author assumes that the carbon points fuse to the transparent modification of carbon, which, like other transparent substances, is a non-conductor of electricity. Owing to the interruption of the current, the temperature falls and the transparent carbon changes into graphite, whereupon the process is repeated.

In order to obtain the transparent fused carbon in the solid form, it appears necessary to cool it so quickly that the transformation into graphite cannot take place. Attempts to obtain rapid cooling by means of hydrogen gas and by dropping the fused carbon into water were unsuccessful owing to the difficulty of obtaining a sufficiently rapid flow of gas in the first case and to the occurrence of Leidenfrost's phenomenon in the second.

By allowing water, under a pressure of about 2200 atmospheres, to rush into the vessel containing a fused mixture of carbon and iron, a piece of iron was obtained about 30 mm. in diameter and so brittle that it could be powdered between the fingers. When dissolved in acid, it left a greyish, crystalline powder of the hardness and specific gravity of diamond.

In conclusion, it is pointed out that the formation of natural diamonds has probably taken place by the sudden cooling of carbonaceous materials at a high temperature and under great pressure.

T. E.

**Direct Combination of Chlorine and Carbon.** By RICHARD LORENZ (*Zeit. Elektrochem.*, 1902, 8, 203—204).—The author observed the direct combination of chlorine and carbon in 1893 (*Zeit. angew. Chem.*, 7, 313).

T. E.

**Lithium Silicide.** By HENRI MOISSAN (*Compt. rend.*, 1902, 134, 1083—1087).—When amorphous or crystalline silicon is heated with sodium or potassium in a vacuum at the boiling point of the metal, very little silicide is formed. *Lithium silicide* can be prepared, when silicon (prepared by Vigouroux's method, *Abstr.*, 1895, ii, 222, 263, 447) is heated with lithium in a vacuum for two or three hours, finally at a temperature of dull redness. The excess of lithium can be removed either by treating the product with liquid ammonia, which reacts with lithium, forming lithium ammonium, a substance soluble in liquid ammonia, or by distilling off the lithium at 400—500° under reduced pressure from the silicide. Lithium silicide,  $\text{Li}_6\text{Si}_2$ , forms small, lustrous crystals of a deep indigo-blue, has a sp. gr. 1.12, and is decomposed in a vacuum above 600° into lithium and amorphous silicon. Hydrogen, above 600°, yields, with the silicide, lithium hydride and silicon. When warmed in gaseous fluorine, reaction takes place with incandescence, producing lithium and silicon fluorides; with chlorine, bromine, and iodine, the reaction is similar, but a higher temperature is required before it begins. Heated in air, it burns and melts; in oxygen, much light and heat are developed. It reacts with molten sulphur with great vigour, a lithium polysulphide and a sulphide of silicon being formed; the last-mentioned substance is decomposed by cold water with evolution of hydrogen sulphide. Selenium, tellurium, and phosphorus all attack the silicide with production of incandescence. Arsenic and antimony form crystalline alloys only slowly attacked by cold water. Lithium silicide reduces the oxides of iron, chromium, and manganese, alloys being produced. When the silicide is placed on sulphuric acid, it becomes incandescent, hydrogen sulphide is evolved, and sulphur formed. With nitric acid, it reacts explosively, producing nitrogen peroxide and silica. With hydrochloric acid, the silicide becomes incandescent and then coated with hydrated silica; at low temperatures, or when dilute acid is used, a gas spontaneously inflammable in air is evolved; it burns with a very white flame and deposits amorphous silica; an ethereal solution of hydrogen chloride has no action on the silicide. The reaction with water is very violent; a spontaneously inflammable gas is evolved, and a solution of lithium

hydroxide containing silica in suspension is obtained. If the reaction is moderated by covering the silicide with glycerol, pure hydrogen is evolved. With aqueous solutions of alkalis, only hydrogen is evolved. It appears that water always decomposes the silicide with formation of hydrogen and a hydrogen silicide,  $\text{Si}_2\text{H}_6$ ; the latter is decomposed by alkalis.

K. J. P. O.

**Mixed Crystals of Silver Chlorate and Sodium Chlorate, and their Solutions.** By H. W. FOOTE (*Amer. Chem. J.*, 1902, 27, 345—354)—It has been shown (Abstr., 1901, ii, 19) that when the sulphates of copper and zinc crystallise from aqueous solution depositing mixed crystals of two different forms, the composition of the crystals at the 'mixing limit' changes with change of temperature. It is now found that a similar statement is true in the case of silver and sodium chlorates. Retgers has shown (Abstr., 1890, 1208) that mixed crystals of these salts are readily obtained in two forms, cubes of sodium chlorate containing 11 mols. per cent. of silver chlorate and tetragonal crystals of silver chlorate containing 41.75 mols. per cent. of sodium chlorate. The 'mixing limits' of these two forms have been determined at 12°, 25°, 35°, and 50°; the results are tabulated.

The relation existing between the salts in solution and the mixed crystals has been studied, with the following results. The proportion of sodium chlorate in the dissolved chlorates in a solution is greater than in the mixed crystals from the solution. As the temperature is raised, the percentage of sodium chlorate in the dissolved chlorates becomes more nearly equal to the percentage of this chlorate in the mixed crystals. By recrystallising the mixed chlorates, pure silver chlorate can be obtained, but pure sodium chlorate cannot be obtained in this way since the recrystallised product contains more silver chlorate than the mother liquor.

E. G.

**Conditions of Formation and Stability of the Hydrides and Nitrides of the Alkaline Earths.** By HENRI GAUTIER (*Compt. rend.*, 1902, 134, 1108—1111).—When an alloy of cadmium and strontium is heated in a closed space with hydrogen (compare this vol., ii, 208) absorption of the gas begins at 340°; at 470—570°, gas is again evolved, to be followed by a second absorption at a higher temperature. At 675°, dissociation of the strontium hydride begins. Very similar results were obtained when an alloy of cadmium and barium was heated in hydrogen. Quantitative experiments show that both strontium and barium hydrides absorb hydrogen readily at the ordinary temperature, and become largely increased in volume. When heated at 70—80° in a vacuum, the evolution of this absorbed hydrogen begins. This absorption of hydrogen does not appear to be due to the formation of a second hydride richer in hydrogen. Calcium hydride has not the power of absorbing hydrogen.

The nitrides of these metals can be obtained by heating their alloys with cadmium, but the combination does not begin below 600°; the nitrides are quite stable at 1000°. The hydrides of barium and strontium are able to absorb nitrogen at the ordinary temperature. When heated with nitrogen, replacement of the hydrogen only begins

towards 600°. In the case of calcium, the nitride is not formed below 700°; that is, at a temperature above that (675°) at which the hydride is dissociated.

K. J. P. O.

**Formation of Calcium Carbide.** By VICTOR ROTHMUND (*Chem. Centr.*, 1902, i, 1045; from *Nachr. k. Ges.-Wiss. Göttingen*, 1901, 224—233).—Experiments on the formation of calcium carbide were made in an electric furnace containing a carbon tube surrounded by layers of carbon and magnesia. The mixture of carbon and lime in the proportion of 12:7 was placed in small carbon tubes which were heated in the larger tube. The temperature was estimated by measuring the intensity of the light emitted on Lummer and Pringsheim's scale. The action does not take place when 700 watts or less are used; it begins at 1620°, and corresponds with a partial pressure of the carbon monoxide of one-fifth of an atmosphere. Experiments showed that when calcium carbide is heated with carbon monoxide at temperatures below 1620°, a portion of the carbide is decomposed. The temperature of formation of the carbide may be reduced by decreasing the partial pressure of the carbon monoxide.

E. W. W.

**Behaviour of Magnesium Chloride in River Waters.** By HUGO ERDMANN (*Zeit. angew. Chem.*, 1902, 15, 449—455).—From analyses of water from the River Wipper at various stations and at different periods, it is proved that: (a) the water becomes more concentrated in magnesium chloride in the neighbourhood of the potash salt deposits without the influx of water from manufactories; (b) as the amount of magnesium chloride increases, there is often a decrease in the total quantity of dissolved salts; (c) as the river rises, the hardness increases if the current is sufficiently strong to stir up the heavier aqueous layers lying in the bed of the stream; and (d) when there is no fresh inflow of solutions, the quantity of magnesium chloride decreases at the lower parts of the river. The author discusses the causes which give rise to effect (d), and shows that they are purely chemical and can be reproduced in the laboratory.

J. McC.

**Electrical Preparation of Colloidal Mercury and other Metals.** By JEAN BILLITZER (*Ber.*, 1902, 35, 1929—1935).—Colloidal mercury is obtained by electrolyzing very dilute solutions of mercurous nitrate between electrodes of platinum, zinc, iron, lead, or nickel; it imparts a yellow or brown colour to the solution. The best result is obtained with a 0.004*N* solution of the nitrate, and a current of 0.2—0.3 ampere at 220 volts; the larger the electrodes, other conditions being the same, the more easily is the colloidal metal formed. Pure colloidal mercury is also obtained by carrying out Bredig's method of "pulverisation" with amalgams or precipitates of mercury on wires which are not themselves pulverisable (compare *Abstr.*, 1899, ii, 78). In the same manner, other metals can be "pulverised" which hitherto have not been obtained in the colloidal form, for example, copper, nickel, iron, zinc, and lead; in all cases, the action is facilitated by using a roughened surface and a loose, superficial aggregation.

W. A. D.



**Application of the Phase Rule to the Fusing Points of Copper, Silver, and Gold.** By THEODORE W. RICHARDS (*Amer. J. Sci.*, 1902, [iv], 13, 377—378).—Holborn and Day (*Abstr.*, 1901, ii, 85) found that gold has a very constant melting point, that of silver is inconstant, and copper apparently has two constant melting points. As gold does not dissolve oxygen, its melting point is not liable to fluctuations, but silver absorbs oxygen, and therefore there are two substances present; unless the concentration of the oxygen be determined, the conditions are too few (solid, liquid, and vapour) to determine a fixed point. The melting point of silver varies, therefore, with the amount of dissolved oxygen. In the case of copper, oxidation takes place and the lower constant melting point is that found when the copper is saturated with cuprous oxide; the higher melting point is that found when oxygen is excluded. J. McC.

**Preparation of the Cerite Metals from "Cerium Oxalicum Medicinale."** By C. R. BÖHM (*Zeit. angew. Chem.*, 1902, 15, 372—380).—After the extraction of thorium from monazite sand, the residue is worked up with oxalic acid into *Cerium oxalicum medicinale*, which contains salts of the rare metals as well as of cerium.

A pure cerium salt is obtained by igniting the crude oxalate and dissolving the residue in double the quantity of concentrated nitric acid; ammonium nitrate is added to the solution and ceric ammonium nitrate crystallises out. If too large an excess of nitric acid is present, the double salt does not crystallise well. The whole of the cerium cannot be removed in this way. The mother liquor from the double salt is treated with oxalic acid, the precipitate dried and ignited, and the greater part of the residue dissolved in concentrated nitric acid, the remainder being converted into a suspension in water. The suspension is added to the solution, and the mixture boiled until, when a small portion is filtered off and the filtrate boiled with hydrogen peroxide, a pure white precipitate is obtained on making it alkaline with ammonia. The liquid is then filtered, the filtrate precipitated with oxalic acid, and the oxalate ignited. The oxide so produced is dissolved in nitric acid, ammonium nitrate is added, and the solution evaporated to the crystallising point. Lanthanum ammonium nitrate separates out, and after fifteen crystallisations it can be obtained almost entirely free from praseodymium. Most of the lanthanum is thus extracted, and to remove the remainder the oxalate is again precipitated and the dried salt added to boiling concentrated sulphuric acid. The sulphates, being insoluble in sulphuric acid, settle down; the sulphuric acid is poured off, and the salts are dried by heating in a platinum basin. The anhydrous sulphates are powdered and added to a small quantity of ice water; on warming the solution to about 20°, a precipitate very rich in lanthanum sulphate separates, whilst the didymium salts remain dissolved. By repeating this process, a didymium sulphate can be obtained practically free from lanthanum but containing a small quantity of yttrium metals. The lanthanum may also be conveniently removed by fractionation with ammonia. By crystallisation of the potassium sulphate double salts from potassium sulphate solution, an almost pure didymium salt

can be obtained, and the relative proportions of praseodymium and neodymium determined by spectroscopic analysis. In the residue from the didymium salt, samarium was detected by the spectrum as well as metals of the yttrium series (terbium, yttrium, erbium, and gadolinium).

The proportion of oxides contained in *Cerium oxalicum medicinale* is estimated at: yttrium oxides (yttrium, ytterbium, erbium, terbium, and gadolinium), 0.2 per cent.; cerite oxides, 99.71 per cent. ( $\text{Ce}_2\text{O}_3$ , 51.35;  $\text{La}_2\text{O}_3$ , 24.16;  $\text{Nd}_2\text{O}_3$ , 16.20;  $\text{Pr}_2\text{O}_3$ , 8.00 per cent., and samarium, trace).

J. McC.

**Rare Earths of the Yttrium Group. I.** By LOUIS M. DENNIS and BENTON DALES (*J. Amer. Chem. Soc.*, 1902, 24, 401—435).—The authors have studied various methods of separating the earths of the yttrium group in order to ascertain along what lines different treatments cause the earths to separate. An historical account of this group is also given. The progress of the separation was followed by determining the atomic weight by Gibbs's method (Abstr., 1894, ii, 47) or that of Krüss (Abstr., 1893, ii, 283); these methods, however, have been shown to be infected with an error. The material used was sipylite from Virginia and from Texas, and the spectroscopic examination showed that this contained yttrium, ytterbium, erbium, thulium, holmium, samarium, dysprosium, and possibly didymium. The results obtained from experiments on the fusion of the yttrium group nitrates with alkali nitrates (compare Dennis and Magee, Abstr., 1895, ii, 15) were irregular and gave no indication of a sharp separation by this method. Comparison of the spectrum of the original mixture of chlorides with that of the substance precipitated from solution by hydrogen chloride showed no change of the relative intensities of the lines. Partial decomposition of the chromates does not lead to an appreciable separation. Fractional precipitation of a solution of the nitrates with potassium chromate separates the earths with considerable rapidity, and this method is particularly valuable for obtaining yttria free from the other earths. The first effect of precipitation with potassium oxalate is to weaken the holmium lines in the spectrum. Erbium has the most soluble oxalate and that increases in the mother liquors by fractional precipitation with potassium oxalate. The decomposition voltages of the rare earths are not sufficiently different to permit of a practical separation by fractional decomposition of a solution of the mixed electrolytes by the electric current. Precipitation with magnesia and treatment with potassium azoimide do not lead to effective separation, whilst although separation can be carried out by fractional precipitation with ammonia, it is extremely slow and tedious. A satisfactory separation can be made by fractional extraction of the precipitated hydroxides with ammonium carbonate solution. A quantity of ammonium carbonate solution is used sufficient to dissolve one-fourth of the precipitate, and when the solution is slowly precipitated with dilute acetic acid, a crystalline salt containing only ytterbium, erbium, and a trace of samarium is obtained. By this fractional treatment, terbium and yttrium concentrate at one end of the series, erbium and ytterbium at the other, and the middle fractions contain the holmium, thulium, and dysprosium.

J. McC.

**Melting Point of Manganese.** By W. C. HERAEUS (*Zeit. Elektrochem.*, 1902, 8, 185—187).—Manganese (99 per cent.) was fused in an electrically heated porcelain tube in a current of hydrogen. The metal rested on a bed of pure alumina and the moment of fusion was observed through a telescope, the temperature being given by a thermo-element placed close to the manganese. The melting point found was  $1245^{\circ}$ . In an atmosphere of nitrogen, combination with the metal takes place rapidly at temperatures above  $1210^{\circ}$ . T. E.

**A Reaction of Iron and Steel.** By V. VON CORDIER (*Monatsh.*, 1902, 23, 217—235).—When commercial iron is dissolved in a dilute acid and, during or after the evolution of gas, the solution is made alkaline, a distinct odour of carbylamine may be observed. Pure iron and iron containing carbon only or nitrogen only do not give the reaction. After passing carbon monoxide and nitrogen over pure iron, the reaction is obtained. As a mixture of iron containing carbon and iron containing nitrogen does not give the reaction, and as it is not obtained with a preparation made by mixing iron containing carbon with manganese nitride, the carbon and nitrogen must be in combination in the iron which gives the carbylamine odour. An iron containing 32 per cent. of manganese did not absorb an abnormal amount of nitrogen. By passing the carbylamine obtained from iron into dilute hydrochloric acid and adding platinum chloride, a platinichloride is formed which, under the microscope, closely resembles in appearance ethylamine platinichloride. The formation of formic acid when the carbylamine is passed into dilute sulphuric acid is shown by conversion into carbon monoxide and its detection by the palladium chloride and spectroscopic tests. G. Y.

**Compounds of Iron and Silicon.** By PAUL LEBEAU (*Ann. Chim. Phys.*, 1902, [vii], 26, 5—31).—A detailed account of the properties of the iron silicides and of the constituents of ferrosilicons (compare Abstr., 1901, ii, 317, and this vol., ii, 135, 264). G. T. M.

**Salts of Chromic and Dichromic Acids.** By WILHELM AUTENRIETH (*Ber.*, 1902, 35, 2057—2064).—Silver chromate,  $\text{Ag}_2\text{CrO}_4$ , is formed when excess of a solution of silver nitrate is added to a solution of potassium dichromate. *Silver dichromate*,  $\text{Ag}_2\text{Cr}_2\text{O}_7$ , on the other hand, is obtained when a solution of potassium chromate or dichromate is mixed with a boiling dilute solution of silver nitrate containing excess of dilute nitric acid, or when excess of a solution of chromic acid is added to a boiling solution of silver nitrate, or when silver chromate is digested with warm dilute nitric acid. This salt forms lustrous red, rhombic leaflets; frequently, however, it is obtained darker in colour, and then very closely resembles iodine; it is decomposed by cold water into chromic acid and silver chromate, which, when thus formed, consists of dark green, or nearly black, rhombic crystals. By heating the red amorphous form of silver chromate in a stream of carbon dioxide, it is converted into the dark green variety.

*Barium dichromate*,  $\text{BaCr}_2\text{O}_7$ , can be prepared by heating together

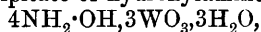
moist barium chromate and chromium trioxide; it crystallises in slender needles, and is decomposed by water into chromic acid and barium chromate. No evidence of the existence of barium trichromate was found, or of that of lead dichromate (compare Preis and Rayman, *Abstr.*, 1880, 444).

Chromium trioxide reacts vigorously with dry hydrogen chloride, forming only chromium oxychloride. Aqueous hydrochloric acid (35—40 per cent.) gives also chromium oxychloride, 35 per cent. of the chromic acid used distilling over. With more dilute hydrochloric acid (20 per cent.), chlorine is formed as well as the oxychloride.

K. J. P. O.

**Oxides of Tungsten.** By EUGENE T. ALLEN and V. H. GOTTSCHALK (*Amer. Chem. J.*, 1902, 27, 328—340).—When tungstic acid is heated with an acid solution of stannous chloride, it undergoes reduction with formation of an insoluble *hydroxide*,  $W_5O_{14} \cdot H_2O$ . The same compound is obtained by heating tungstic acid with fuming hydriodic acid at 200° in a sealed tube. It forms a dark blue powder with a purplish lustre; it is insoluble in water acidified with hydrochloric acid, but in pure water it seems to form a colloidal solution. It is readily oxidised by exposure to the air or by oxidising agents, and is instantly converted into the trioxide by the action of heat. When heated with a solution of an alkali hydroxide, hydrogen is evolved and a tungstate is produced, whilst by the action of ammonia, ammonium tungstate and a brown residue are formed, but no gas is evolved. This brown residue is a *hydroxide* of the composition  $W_8O_8 \cdot H_2O$ ; when washed and dried, it has a deep purple colour with a bronze lustre; in its chemical behaviour, it resembles the blue compound.

If hydroxylamine hydrochloride is added to a solution of sodium tungstate, a white precipitate of hydroxylamine *tungstate*,



is produced, which when dry is of a pale yellow colour.

E. G.

**Uranium Sulphates.** By WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1902, 94—97, 161—163. Compare *Abstr.*, 1901, ii, 390, 556).—The author has determined the solubilities of uranic and uranous sulphates in various media, and finds that one part of each of the solvents named below dissolves the following quantities of these salts at the temperatures mentioned :

Uranic sulphate—

Alcohol, 85 per cent. ....	37.9 at 16.7°	38.6 at 15.8°
Hydrochloric acid (conc.) .....	3.4 „ 12.8	3.25 „ 13.6
Hydrobromic acid of sp. gr. 1.21... ..	5.9 „ 12.9	6.1 „ 11.2
Nitric acid (conc.) .....	10.8 „ 12.3	11.2 „ 10.8
Sulphuric acid of sp. gr. 1.138 .....	4.3 „ 12.7	4.1 „ 14
Nitric acid and water (equal volumes) .....	5.6 „ 15.4	5.47 „ 16.4
Sulphuric acid and water, 1 : 4.....	3.7 at 15.3	

The salt is slightly soluble in formic and acetic acids.

## Uranous sulphate—

Water .....	4.23 at 13°	4.3 at 11.3°	4.4 at 9.1°
Hydrochloric acid and water, 1:4 .....	—	5.74 „ 9.7	5.8 „ 9.2
Nitric acid and water, 1:4 .....	—	5.4 „ 11.2	5.53 „ 10.3
Selenic acid of sp. gr. 1.4 and water 1:4...	—	4.57 „ 11.4	4.66 „ 10.7
Alcohol (94 per cent.) and water, 1:4 ...	—	8 „ 10.4	8.2 „ 9.6

The aqueous solutions in the order mentioned deposited small quantities of a basic sulphate after 24, 30, and 38 hours respectively.

Sulphuric acid  
and water,

1:4 ..... 6.36 at 11.7° 6.42 at 10.9° 6.45 at 10.1° 6.5 at 9°

## Hydrobromic

acid and

water, 1:4 4 „ 15 4.23 „ 14.2° — —

## Acetic acid

and water,

1:4.5 ..... 4.1 „ 15.5 4.3 „ 14.4° — —

## Acetic acid

and water,

1:2 ..... 3.72 „ 16.5 3.85 „ 15.9° — —

When solutions of uranic (or uranous) sulphate are hydrolysed in a U-tube cooled by immersion in water, there is first deposited on the negative electrode the yellow, hydrated oxide,  $U_2O_3 \cdot 2H_2O$ , and finally a greenish precipitate consisting of the oxide and a small proportion of a basic sulphate. In the absence of the cooling medium, the black oxide,  $U_4O_9$ , is formed. When aqueous alcoholic solutions of uranic sulphate are exposed to light, a mixture of uranous sulphate with a small quantity of basic uranic sulphate is deposited. The filtrate, on exposure to violet or blue light, forms at first a hydrated uranoso-uranic oxide, and eventually the black oxide,  $U_4O_9$ . T. A. H.

**Electrolysis of Potassium Antimony Tartrate.** By FRANZ VON HEMMELMAYR (*Monatsh.*, 1902, 23, 262—268. Compare Böttger, *J. pr. Chem.*, 1856, 68, 372).—Electrolysis of a saturated solution of potassium antimony tartrate or of sodium antimony tartrate results in the deposition of antimony mixed with small quantities of antimony trioxide. Marchand's suboxide,  $Sb_3O_2$ , is not formed. G. Y.

## Mineralogical Chemistry.

**A New Association of Gold.** By HENRY F. COLLINS (*Zeit. Kryst. Min.*, 1902, 36, 92; from *Eng. & Mining J.*, 1900, 69, 464).—Crystals of bornite in wollastonite from the Santa Fe mine, Chiapas, Mexico, gave on analysis the results under I. The gold [ $\frac{1}{2}$  0.00333 per cent.] for the most part cannot be amalgamated, and is probably present as sulphide. The ore, where richest in gold, is intergrown with garnet, copper-pyrites, a little galena, enargite, &c.

Massive bornite from the upper workings of the mine sometimes contains nodules and grains of siegenite, which gave the results under II (As, Sb, Bi, Ti are absent).

	Cu.	Ag.	Au.	Fe.	Ni.	Co.	S.	Insol. (quartz).	Total.
I.	62.1	0.2	0.0333	—	—	—	—	—	—
II.	5.32	0.13	0.53	3.32	17.15	29.64	44.31	0.43	100.83.

L. J. S.

**Minerals Occurring in Australian Bat Guano.** By R. W. EMERSON MACIVOR (*Chem. News*, 1902, 85, 181—182, 217. Compare Abstr., 1887, 708—709).—Further confirmatory analyses of hannayite, newberyite, and struvite are given, as well as descriptions of the other constituents of bat guano alluded to in his previous communication. *Dittmarite*,  $\text{MgNH}_4\text{PO}_4 \cdot 2\text{Mg}_2\text{H}_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , occurs as small, transparent, rhombic crystals. Analysis gave :

MgO.	FeO.	MnO.	$(\text{NH}_4)_2\text{O}$ .	$\text{P}_2\text{O}_5$ .	Water.
25.67	0.38	0.08	3.94	46.51	23.42

*Schertalite* (for which the name muellerite, already in use, was first suggested) occurs in small, flat crystals of somewhat indistinct character, with difficulty freed from adhering and included guano. They lose water of crystallisation at  $120^\circ$ , but not at  $100^\circ$ , and on ignition yield magnesium metaphosphate. Analysis gave :

MgO.	FeO.	MnO.	$(\text{NH}_4)_2\text{O}$ .	$\text{P}_2\text{O}_5$ .	$\text{H}_2\text{O}$ .
12.17	0.20	0.05	16.15	43.88	27.55

corresponding with the formula  $\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ . The “drier” guano deposits in which these various constituents occur contains : water, 19.80; organic matter, 52.83; ash, 27.37 per cent. The organic matter contains 2.98 of nitrogen nearly all as nitrate; the ash contains :

$\text{Fe}_2\text{O}_3$ .	$\text{Al}_2\text{O}_3$ .	CaO.	MgO.	$\text{Na}_2\text{O}$ .	$\text{K}_2\text{O}$ .	$\text{P}_2\text{O}_5$ .	$\text{SO}_3$ .	$\text{SiO}_2$ (sol.).	$\text{CO}_2$ .	Insoluble.	Mn.
5.23	2.00	0.58	2.93	1.79	5.38	1.57	1.06	2.00	3.65	trace	

Reference is made to a white, nodular constituent, apparently consisting mainly of tribasic magnesium phosphate, which will be more fully described later.

D. A. L.

**Formation of Oceanic Salt Deposits, particularly of the Stassfurt Beds. XXVI. Formation of Loeweite and the Lower Temperature Limit of the same at 43°.** By JACOBUS H. VAN'T HOFF and A. O'FARRELLY (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 370—375).—Dilatometric experiments show that astracanite,  $\text{MgSO}_4, \text{Na}_2\text{SO}_4, 4\text{H}_2\text{O}$ , is transformed into loeweite,  $\text{MgSO}_4, \text{Na}_2\text{SO}_4, 2\text{H}_2\text{O}$ , at 71°, and this result is confirmed by comparing the tensions at various temperatures of (1) a dry mixture of loeweite and astracanite, and (2) a mixture of astracanite with 2 mols. of water. When a solution of sodium and magnesium sulphates in molecular proportion is evaporated at a temperature above 71°, astracanite is first obtained, but this is transformed into loeweite on contact with the mother liquor and inoculation with a small quantity of partially dehydrated astracanite. The temperature of transition of astracanite into loeweite is lowered in presence of other soluble salts, such as sodium chloride, and reaches its lower limit at 43°. The paper contains also determinations of the tension of the water of crystallisation in astracanite at various temperatures between 25° and 71°, and an equation is obtained which expresses satisfactorily the relation between the vapour tensions of water and astracanite over this range. The process represented by the equation  $\text{MgSO}_4, \text{Na}_2\text{SO}_4, 2\text{H}_2\text{O} + 2\text{H}_2\text{O} = \text{MgSO}_4, \text{Na}_2\text{SO}_4, 4\text{H}_2\text{O}$  is accompanied by the evolution of 6600 cal. J. C. P.

**Minerals from the Pacific States.** By HENRY W. TURNER (*Amer. J. Sci.*, 1902, [iv], 13, 343—346).—Brief notes are given of the occurrence of the following less common minerals in the United States east of the Rocky Mountains: pyromorphite, monazite, apatite, vivianite, chloropal, diopside, idocrase, jarosite and nickel minerals (perhaps gersdorffite and genthite).

The apatite, as a constituent of gneiss in the Sierra Nevada, appears to be neither a fluoro- nor a chloro-apatite. The golden-brown micaceous mineral from Nevada, referred to jarosite, differs from this in containing sodium (nearly 6 per cent.) instead of potassium. Idocrase from limestone at its contact with granite in the Silver Peak quadrangle, gave on analysis by G. Steiger:

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{FeO}$	$\text{CaO}$	$\text{MgO}$	$\text{Na}_2\text{O}, \text{K}_2\text{O}$	$\text{H}_2\text{O}$	$\text{TiO}_2$
36.80	17.53	3.27	1.56	35.00	1.23	0.13	1.66	0.66
Total								
$\text{CO}_2$	$\text{P}_2\text{O}_5$	$\text{SO}_3$	Cl.	F.	MnO.	BaO.	less O for F.	
0.65	0.07	nil	nil	0.88	0.48	nil	99.56.	

Partial analyses are given of the chloropal and diopside. L. J. S.

**Fusion Point of Minerals and the Petrographic and Synthetic Conclusions derived from the Results.** By A. BRUN (*Arch. Sci. phys. nat.*, 1902, [iv], 13, 352—374).—The melting point was determined in a specially constructed furnace, a chip of the mineral being supported inside on the top of a small platinum tube across which a thin wire was stretched; the temperature was registered by means of Seger cones. The fusion point of basic silicates is very definite;

acid silicates persist in a semi-solid condition for a considerable time. The melting points of various minerals belonging to the amphibole group, the feldspar group, and the pyroxene group were determined as well as those of various other minerals.

The author applies his results to the solution of certain geological problems in connection with the temperature of the lava ejected from volcanoes, and the determination of the conditions of the crystallisation of rocks. The greater part of the mineral matter of a basic lava is produced at a temperature between  $1200^{\circ}$  and  $2000^{\circ}$ . In the formation of acid rocks, the first stage is the production of a colloidal hydroxide which can withstand the temperature of  $830^{\circ}$ ; on cooling to  $800^{\circ}$ , reaction takes place between this hydroxide and the acid silicates present. This theory satisfactorily accounts for the presence of liquid inclusions contained in the quartz of a granite, and the presence of micas containing fluorine.

J. McC.

[Pyroxene, Labradorite and Pseudomesolite from Minnesota.] By ALEXANDER N. WINCHELL (*Zeit. Kryst. Min.*, 1902, **36**, 70—72; from *Amer. Geol.*, 1900, **26**, 151—188, 197—245, 261—306, 348—388; and *Thèse Fac. des Sci. Paris*, 1900).—The following mineral analyses are given in a petrographical description of the gabbros, &c., of Minnesota. I, Pyroxene from olivine-diabase at Pigeon Point; the optic axial angle is small and variable in size ( $2E = 13^{\circ}16' - 62^{\circ}24'$ ), and on account of this abnormal character the name *pigeonite* is proposed. II, Labradorite ( $Ab_3An_4$ ) from anorthosite at Carlton Peak; crystallographic and optical determinations are given. III, *Pseudomesolite* in radially fibrous masses which are colourless or white; it is probably triclinic and resembles mesolite in chemical composition, but differs from this in optical characters:

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.
I.	45.05	4.39	0.16	5.50	14.90	1.58	10.72
II.	53.38	—	29.70	0.21	—	—	11.90
III.	45.25	—	25.69	1.40	—	—	9.75

	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.	Sp. gr.
I.	15.15	0.78	1.27	0.13	99.63	—
II.	trace	0.56	4.30	0.37	100.42	2.701
III.	trace	0.47	4.24	12.99	99.79	2.219

L. J. S.

[Analysis of Talc, Halloysite and Lenzinite.] By GEORGE P. MERRILL (*Zeit. Kryst. Min.*, 1902, **36**, 73; from *Rep. U. S. National Museum* for 1899, 1901, 155—483).—A "Guide to the Study of the Collections of the Section of Applied Geology (the Non-metallic Minerals)" in the United States National Museum, gives descriptions of the useful minerals, with notes on their modes of origin, localities and applications. Numerous analyses are given, of which the following are new. I—VI, Steatite from various localities in the United States. VII, Halloysite from Edwards Co., Texas. VIII, Soap-stone (lenzinite) from Ventura Co., California.



	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO.	MgO.	CaO.	MnO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	42.43	6.08	13.07	25.71	3.27	trace	0.16	0.32	8.45	99.49
II.	51.20	5.22	8.45	26.79	1.17	0.32	—	—	6.90	100.05
III.	38.37	5.64	8.86	28.62	3.90	trace	—	—	14.49	99.88
IV.	52.70	5.57	7.63	26.88	1.77	—	—	—	5.48	100.03
V.	40.03	10.86	9.59	26.97	1.70	—	—	—	10.78	99.93
VI.	33.47	0.45	7.38	32.72	1.34	0.21	—	—	23.00	99.57
VII.	45.82	39.77	—	—	—	—	—	0.30	18.38	99.27
VIII.	67.55	12.97		0.85	0.77	—	3.63	1.43	13.67	100.87

L. J. S.

**Anorthite and Epidote.** By WILLIAM F. HILLEBRAND (*Bull. U.S. Geol. Survey*, 1900, No. 167, 69—70).—Specimens of metamorphic limestone from Phippsburg, Maine, with much cinnamon garnet and a little green pyroxene, contain here and there, embedded in the masses of garnet, brilliant plates of a dark gray to nearly black mineral, which is shown by the following analysis (I) to be epidote, although it does not present the usual appearance of this mineral; the determination as epidote was confirmed under the microscope. Associated with the epidote is anorthite (anal. II. by G. Steiger).

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO.	CaO.	MgO.	Ignition.	Total.
I.	38.54	28.39	6.89	0.50	24.12	trace	2.26	100.70
II.	45.62	35.29	—	—	17.31	—	—	98.22

L. J. S.

[**Bytownite and Diopside from Maine.**] By E. C. E. LORD (*Zeit. Kryst. Min.*, 1902, 36, 72; from *Amer. Geol.*, 1900, 26, 329—347).—The following mineral analyses are given in notes on the geology and petrology of Monhegan Island, Maine. (I) Bytownite (AbAn<sub>6</sub>) from olivine-norite. (II) Diopside from gabbro-pyroxenite.

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.	Sp. gr.
I.	48.06	—	32.54	—	17.51	—	—	1.77	—	—	99.88	2.72
II.	40.61	0.65	25.90	2.18	5.37	14.50	7.69	0.25	2.31	0.78	100.24	2.91

L. J. S.

[**Allophane ? from Kansas.**] By AUSTIN F. ROGERS (*Zeit. Kryst. Min.*, 1902, 36, 79—81; from *Kansas Univ. Quart.*, 1900, 9, 161—165).—A list is given of the minerals found in the zinc and lead district of Joplin in Missouri and Kansas. Allophane (?) occurs as a thin coating on zinc-blende at Galena in Kansas; it is amorphous, translucent, colourless to pale-brown or green, and with a resinous lustre; analysis gave:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O.	Total.	Sp. gr.
24.76	[41.66]	33.58	100.00	1.94

L. J. S.

**Meteoric Irons.** By EMIL W. COHEN (*Ann. k.k. naturhist. Hofmus. Wien*, 1900, 15, 351—391).—In No. XI of his *Meteoric Iron Studies*, the author gives the results of the examination of 19 irons, with numerous analyses of the irons as a whole and of the various minerals (cohenite, schreibersite, t  nite, amorphous carbon and cliftonite) isolated from them.

L. J. S.

## Physiological Chemistry.

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**Hereditary Transmission of Hæmolysins.** By WILLIAM BULLOCH (*Trans. Path. Soc.*, 1902, 53, 189—196).—Hæmolysins were produced in rabbits by injecting blood-corpuscles of the ox; the characters of the blood of the offspring were examined. The hæmolytic power is not transmitted by the male if the mother is normal. If the mother was rendered immune after conception, abortion occurred, but the foetal blood was highly hæmolytic. If the mother was immunised before conception, the serum of the offspring was more hæmolytic than that of the mother, owing to its containing a greater quantity of the complement. The immune substance also passes out in the milk, but in diminishing quantities in successive litters. Hæmolysins are demonstrable in the blood of the young four months after birth. The results coincide with those obtained by Ehrlich with ricin and tetanus. W. D. H.

**Hæmolysin of Bacillus Megatherium.** By CHARLES TODD (*Trans. Path. Soc.*, 1902, 53, 196—214).—In cultures of *B. megatherium* a specific lysin occurs which hæmolyses the corpuscles of guinea-pig, monkey, and man. In guinea-pigs, this is sufficient to cause hæmoglobinuria and death. It is destroyed by heating to 56° for half-an-hour. The formation of the lysin takes place best in alkaline broth at 37°. The normal serum of many animals exercises an anti-hæmolytic power towards this lysin, and this action is increased by heating at 63° for half-an-hour. Subcutaneous injection of the lysin gives rise to a powerful anti-hæmolysin. By partial neutralisation, the lysin yields a characteristic spectrum, as was shown by Ehrlich with tetanus lysin and diphtheric toxin. The lysin is also divisible into parts named prototoxin (a toxoid), deuterotoxin, tritotoxin, and a fourth substance of the nature of a toxone. W. D. H.

**Does Lipase Exist in the Serum?** By DOYON and MOREL (*Compt. rend.*, 1902, 134, 1002—1005).—Normal serum, if aseptic, contains no ferment which splits or saponifies olein. W. D. H.

**The Substitution of Chlorine by Bromine.** By T. HONDO (*Chem. Centr.*, 1902, i, 1118; from *Berlin Klin. Woch.*, 39, 205—209).—With an ordinary mixed diet, bromine salts are rapidly eliminated; still traces remain for months. If, however, insufficient sodium chloride is given, the elimination is much slower. There is no marked influence on metabolism if the lessening of sodium chloride is not continued too long. In the treatment of such maladies as epilepsy with bromides, the lessening of the common salt in the diet is therefore recommended. W. D. H.

**Feeding Experiments with Chondroitinsulphuric Acid.** By A. KETTNER (*Chem. Centr.*, 1902, i, 1020; from *Arch. exp. Path.*

*Pharm.*, 47, 178—199).—Amyloid substance is a combination of proteid and chondroitinsulphuric acid. Oddi found that feeding animals with this acid did not produce amyloid degeneration. In the present experiments on rabbits, an acid nutriment was first given, and then hydrochloric acid and sodium chondroitinsulphate. The animals suffered from acid poisoning but nothing further. Chondroitinsulphuric acid is not affected by gastric or pancreatic juices, so its destruction is a metabolic process. Long continued acid poisoning in rabbits causes no increase in the excretion of ammonia by these animals. The difference between the dog and the rabbit in this direction is believed to be absolute, not relative. W. D. H.

**Non-absorption of Antitoxin from the Stomach and Rectum.** By RICHARD TANNER HEWLETT (*Trans. Path. Soc.*, 1902, 53, 220—221).—The experiments were made on rabbits and guinea-pigs with the antitoxin of diphtheria and tetanus. No trace of either is absorbed by the mucous membrane of the stomach or of the rectum. W. D. H.

**Purine Substances in Articles of Diet.** By J. WALKER HALL (*Chem. Centr.*, 1902, i, 1169—1170; *Inaug. Diss. Owens Coll. Manchester*).—An extension of the work of Burian and Schur (*Abstr.*, 1897, ii, 333) on the amount of purine nitrogen in numerous articles of diet. A modification of their method of estimation is proposed, in which the relative volume of the silver precipitate is measured. W. D. H.

**Contact Irritability of Muscles.** By W. D. ZOETHOUT (*Amer. J. Physiol.*, 1902, 7, 320—324).—If the calcium salts in the muscle are decreased, the efficiency of potassium ions to increase its tone is increased. If the potassium ions in the muscle are increased, the efficiency of such salts as sodium oxalate and citrate to cause contact-irritability is increased. Contact irritability depends, as Loeb suggested, on the disturbance of the normal ratio of salts in the muscle. Perhaps it is the disturbed ratio between the potassium and the calcium salts which makes the contact reaction possible. W. D. H.

**Diastatic Ferment of the Suprarenal Body.** By ALFRED C. CROFTAN (*Pflüger's Archiv*, 1902, 90, 285—289).—Solutions of the precipitate produced by saturating extracts of suprarenal capsules with ammonium sulphate have a diastatic action, converting starch into maltose and, later, into dextrose. Both a maltase and a glucase are therefore present. Arguments are adduced in favour of the existence of such a disease as suprarenal glycosuria. W. D. H.

**Influence of Lecithin on the Development of the Skeleton and Nervous System.** By ALEXANDRE DESGREZ and ALY ZAKY (*Compt. rend.*, 1902, 134, 1166—1168).—The administration of lecithin in animals produces a retention of phosphoric acid, which is normally utilised for the development of bone and nerve tissue. The increase of lecithin in the nervous system is not directly due to the lecithin given, but to that synthetically formed in the animal. W. D. H.

**Variations in the Composition of Cows' Milk during Milking.** By EDWIN ACKERMANN (*Milch-Zeit.*, 1902, 31, 166—168).—The usual statement, that the percentage of fat in milk increases gradually as the milking proceeds, was not found to be correct, according to the experiments described in this paper. It was ascertained, however, that, by milking the teats singly or in pairs, the fat showed an increase up to a maximum at the end of the milking. On drawing the milk from the second pair of teats, the amount of fat at the commencement was slightly more than that given by the first pair, and rose at the end to a higher maximum. The increase is possibly due to mechanical or physiological stimulus.  
W. P. S.

**Nitrogenous Metabolism in a Case of Bright's Disease.** By J. A. BUTLER and A. S. FRENCH (*Trans. Path. Soc.*, 1902, 53, 236—274).—The patient was a child who suffered from acute parenchymatous nephritis. If the proteid of the urine is not reckoned, the proportion of nitrogen excreted as urea was normal, but if the proteid is included, it was less than in health. This holds good for both uræmic and non-uræmic periods. The uræmic period was marked by an output of nitrogen in excess of the intake, and a high and almost constant ratio of uric acid to urea. The amount of nitrogen in the fæces was greater than in healthy children on a milk diet.  
W. D. H.

**Chylous and Chyliform Ascites.** By ROBERT HUTCHISON (*Trans. Path. Soc.*, 1902, 53, 274—276).—Cases are described of both these varieties of ascites. In the true chylous ascites, the milky appearance is due to fat, presumably from ruptured lacteals. In the chyliform variety, the fluid appears like a solution of glycogen. Fat, lecithin, and mucoid are absent; the opalescence is ascribed to some form of nucleo-proteid. Such fluids have no special significance and are met with in various pathological conditions.  
W. D. H.

**Glycosuria of Muscular Origin.** By CADÉAC and MAIGNON (*Compt. rend.*, 1902, 134, 1000—1002).—Crushing injuries to muscles in guinea-pigs, dogs, and men causes the appearance in the urine of sugar and, to a greater extent, of glycuronic acid. These substances are of muscular origin, and are found in extracts of the injured muscles, but not in those of healthy muscles.  
W. D. H.

**Low Proteid Metabolism.** By VAUGHAN HARLEY and FRANCIS GOODBODY (*Trans. Path. Soc.*, 1902, 53, 228—235).—Full details are given of patients suffering from obesity and neurotic disturbances, who maintained approximate equilibrium on an extremely small amount of proteid nutriment.  
W. D. H.

**Chemical Constitution and Physiological Action.** By MARC LAFFONT (*Compt. rend.*, 1902, 34, 861—863).—Accordingly as arsenic is united to one or two methyl groups, its toxicity varies from one to five. In therapeutic purposes, the monomethyl compound is preferable if given by the mouth; the dimethyl compound acts more rapidly and is not decomposed in the blood; it should be given hypodermically.

In the case of the substituted derivatives of the benzenoid hydrocarbons, the group which most completely masks the toxic action of the original hydrocarbon or even that of its phenolic derivative (phenol guaiacol) is  $\text{SO}_3\text{H}$ ; thus in the compound  $\text{C}_6\text{H}_5\cdot\text{SO}_3\text{H}$  the benzene is rendered inoffensive and invigorating.

W. D. H.

**The Power of the Sulphate to neutralise the Ill Effects of the Chloride of Sodium.** By ANNE MOORE (*Amer. J. Physiol.*, 1902, 7, 315—319).—The experiments were made on tadpoles and mosquito larvæ. Loeb found that the toxic effect of salts with a univalent cation and a univalent anion can be annihilated by bi- or ter-valent cations, but not by uni-, bi-, or ter-valent anions. The present results with sodium sulphate and chloride show that it is possible in one case at least to annihilate the poisonous effects of a salt of this character by a bivalent anion. Sodium oxalate, however, has not the same effect. The explanation is not yet evident.

W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Production of Parasitic Races from Common Bacteria.** By L. LÉPOUTRE (*Compt. rend.*, 1902, 134, 927—929).—It was shown by Laurent (*Ann. Inst. Pasteur*, 1899, 13), that *Bacillus coli communis* and *B. fluorescens putridus*, which are normally harmless, may be transformed into very active parasites of potatoes and carrots.

Carrots from plots manured with excessive amounts of nitrogen, potassium, superphosphate, calcium carbonate, and sodium chloride respectively were inoculated with *Bacillus fluorescens liquefaciens*, *B. mycoides*, and *B. mesentericus vulgare* and kept at 30°. *B. fluorescens* proved to be the most active, especially on the roots manured with nitrogen and with calcium carbonate. Cultivations of all three bacilli were, however, obtained which possessed the power of living as parasites on the carrots of all the plots. The roots of the superphosphate plot were the most resistant. Similar results were obtained when turnips were inoculated with the parasitic microbes.

Feeding roots resisted the action of the bacilli, which, however, rapidly attacked the roots after treatment for an hour with 0·1 per cent. soda.

Two actions are shown to take place, one due to a diastase, *pectinase*, which dissolves pectic substances, and the other to a substance which coagulates protoplasm. Pectase is destroyed at 62°, whilst the coagulating substance resists a temperature of 100°. N. H. J. M.

**Butyric Fermentation. Occurrence and Biological Relations of the mobile Butyric Bacillus.** By ARTHUR SCHATTENFROH (*Arch. Hygiene*, 1902, 42, 251—264).—This bacillus is strictly anaërobic and only grows well in solutions containing soluble fermentable carbo-

hydrates and organic nitrogenous substances. It scarcely attacks proteid substances, although it requires them for growth, but ferments mono- and di-saccharides, starch, and glycerol, whilst it has no action on mannitol and on lactates. The products of the fermentation of the carbohydrates are butyric acid, lactic acid, carbon dioxide, and hydrogen, but the proportions in which they are produced vary considerably. In only one case was butyl alcohol produced. The ratio of lactic to butyric acid is also very variable, and whereas some strains of the organism produce *i*-lactic acid, others produce the *d*-acid. The bacillus does not produce any proteolytic enzyme in the media in which it is cultivated, but regularly produces an amylase, whilst sucrase was found on one occasion.

A. H.

**Rancidity of Butter.** By ORLA JENSEN (*Centr. Bakt. Par.*, 1902, 8, ii, 11—16, 42—46, 74—80, 107—114, 140—144, 171—174, 211—216, 248—252, 278—281, 309—312, 342—346, 367—369, 406—409).—When butter is exposed to sunlight in presence of oxygen, the latter is absorbed, the iodine number of the butter fat diminishes, and the butter acquires an unpleasant odour and taste, but in the absence of micro-organisms there is scarcely any production of free acid, and the butter does not become rancid. True rancidity is caused by various micro-organisms, all of which are aerobic, so that the rancidity spreads from the outside inwards. The chief organisms concerned are *Oidium lactis*, *Cladosporium butyri*, *Bacillus fluorescens liquefaciens*, and sometimes *B. prodigiosus*, the ordinary lactic acid-producing organisms taking no part in the phenomenon. These organisms of rancidity decompose the butter fat, probably by means of a steapsin, although this is not quite certain, with the production of both volatile and non-volatile acids. In addition to this, *Cladosporium* has the power of producing butyric esters, the alcoholic radicle being most probably supplied by decomposition products of the glycerol set free from the decomposed fats. The two moulds, however, exert a destructive action on the volatile fatty acids and tend to diminish their amount. The addition of milk sugar to the butter diminishes the production of esters, whilst the addition of salt chiefly diminishes the amount of volatile acids. The action of the organisms which produce rancidity is considerably diminished by the presence of bacilli of the lactic acid group, the lactic acid produced being probably the active substance.

A. H.

**Fermentation of Cellulose.** By V. OMELIANSKI (*Centr. Bakt. Par.*, 1902, 8, ii, 193—201, 225—231, 257—263, 289—294, 321—326, 353—361, 385—391. Compare *Abstr.*, 1896, ii, 202; 1898, i, 291; 1900, ii, 493).—Two species of bacilli have been found which bring about a fermentation of cellulose, and these occur very widely in soil, manure, sewage deposits, river mud, &c. They cannot be isolated in the ordinary way as they do not grow on solid media, and the method of accumulation was therefore employed. Neither of these species is identical with the *Bacillus amylobacter*, which, according to van Tieghem, is the chief organism which attacks cellulose. The first species brings about a hydrogen fermentation of cellulose, 3.22

grams of the latter being converted into 0.014 gram of hydrogen, 0.9722 gram of carbon dioxide, and 2.24 grams of fatty acids, consisting of a mixture of 1 part of butyric acid with 1.7 parts of acetic acid.

The second species brings about the methane fermentation of cellulose, the products derived from 2.03 grams of the latter being 0.14 gram of methane, 0.87 gram of carbon dioxide, and 1.02 grams of fatty acids, consisting of a mixture of 1 part of butyric acid with 9 parts of acetic acid. Both the species grow best at 35–40°. A. H.

**Formation of Oxalic Acid by Bacteria.** By FRIEDRICH BANNING (*Centr. Bakt. Par.*, 1902, ii, 8, 395–398, 425–431, 453–456, 520–525, 556–567).—Eight new species of oxalic acid forming bacteria have been found, so that in all 15 species are known which have this function. The effect of all these has been tried on a large number of organic substances added to solid media, and the culture then examined qualitatively for oxalic acid. Of the carbohydrates examined, it was found that oxalic acid was formed from dextrose by all the 15 species, from arabinose by 11, from hævulose, galactose, maltose, sucrose, milk-sugar, raffinose, rhamnose, *isolichenin*, and dextrin by only a few of the species, and from starch, inulin, glycogen, and gum arabic by none. Among the alcohols, oxalic acid was formed from ethylene glycol, and from glycerol by 8 species, from erythrol by 7 species, from ethyl alcohol by 4 species, from mannitol by 3 species, and from methyl, propyl, butyl, and amyl alcohols and dulcitol by none. Of the acids, oxalic acid was formed from pyrotartaric acid by 9 species, from glycollic acid by 8 species, from malonic acid by 5 species, from acetic and *isobutyric* acids by 3 species, and from formic acid, propionic acid, butyric acid, valeric acid, succinic acid, malic acid, tartaric acid, citric acid, glycine, sarcosine, and leucine by none. None of the species was able to produce oxalic acid from urea, uric acid, creatine, creatinine, benzoic acid, hippuric acid, salicylic acid, or tyrosine.

A. H.

**Products of the Fermentation of Sucrose by a Mucus-forming Bacillus, and the Composition of a Carbohydrate isolated from the Mucus.** By FRANZ SCHARDINGER (*Centr. Bakt. Par.*, 1902, ii, 8, 144–147, 175–181).—The bacillus, which was isolated from an impure drinking water and appears to be closely allied to *Bacillus lactis pituitosi*, Loeffler, has the power of rendering media, both with and without sugar, slimy or ropy. When cultivated in sucrose solution in presence of ammonium chloride and inorganic salts together with calcium carbonate to neutralise the acid produced, the sucrose is decomposed, hydrogen being evolved, and alcohol, acetic acid, succinic acid, and *l*-lactic acid produced, the last-named being the chief product. The mucus or slime may be isolated by evaporating in a vacuum, precipitating with alcohol, dissolving in very dilute alcohol, filtering, and then repeatedly precipitating with alcohol and redissolving in water, about 6.5 grams being finally obtained from 50 litres of culture medium. It forms a white mass which is free from nitrogen and has the composition  $C_6H_{10}O_5$ . It is optically inactive and forms an oily



solution in water, which is not ropy but becomes gelatinous at low temperatures. Distillation with hydrochloric acid produces furfuraldehyde, whilst oxidation converts the substance into oxalic and mucic acids. Acid hydrolysis yields a dextrorotatory sugar the exact nature of which has not yet been ascertained. The substance isolated is probably a galactan and does not itself appear to be the cause of the ropiness of the culture solutions. Further investigations on this point are in progress. A. H.

**Denitrification.** By HUGO WEISSENBERG (*Centr. Bakt. Par.* 1902, ii, 8, 166—170. Compare *Arch. Hygiene*, 30, 274).—The decomposition of nitrates observed by Wolf (*Hygienische Rundschau*, 9, 518, 1169), in solutions containing sugar is largely due to the liberation of nitrous acid by the acid produced from the sugar, followed by the decomposition of the unstable acid, whereas true denitrification proceeds in alkaline solution. When a culture of a denitrifying organism containing nitrite is exposed to air, the same amount of oxygen is absorbed as in a culture free from nitrite, but in the former case the growth of the organism is much more plentiful, owing to the fact that the oxygen of the nitrite is also used. A. H.

**Constituents of the Flowers of the Coffee Tree.** By L. GRAF (*Zeit. öffentl. Chem.*, 1892, 8, 148—150).—The flowers were obtained from trees twenty years old growing in Réunion; they were yellowish-brown and had an intensely bitter taste. They were found to contain caffeine (0.92 per cent.), phytosterol, a reducing sugar, and probably caffetannic acid. N. H. J. M.

**Occurrence of Oleodistearin in the Fat of the Seeds of Theobroma Cacao.** By R. FRITZWEILER (*Chem. Centr.*, 1902, i, 1113; from *Arb. Kais. Ges.-A.*, 18, 371—377. Compare Heise, *Chem. Rev. Fett.-Harz-Ind.*, 6, 91; *Arb. Kais. Ges.-A.*, 13, 302).—Six per cent. of oleodistearin has been isolated from the fat of *Theobroma cacao* after removing the cocoa fat by Heise's method. E. W. W.

**Aroma of Tobacco.** By SIGMUND FRÄNKEL and ALFRED WOGGINZ (*Monatsh.*, 1902, 23, 236—238).—Attention is drawn to nicotianine, an alkaloid obtained from tobacco (Landerer, *Repert. Pharm.*, 53, 205), which has been overlooked by later authors.

On distilling tobacco with steam, a milky distillate, possessing the odour of tobacco, is obtained, from which no crystals separate. It gives precipitates with mercuric chloride, silver nitrate, phosphotungstic acid, lead acetate, and picric acid. The *picrate* forms small, yellow, silky needles, melts at 214°, and is soluble with difficulty in cold and more easily in boiling alcohol or water. G. Y.

**Influence of Iron on the Combustibility of Tobacco.** By G. AMPOLA and S. JOVINO (*Gazzetta*, 1902, 32, i, 367—380).—The authors give a number of analyses of different kinds of tobacco the combustibilities of which were also determined. From the results they conclude that the factors influencing the combustibility of tobacco are

its state of division and the amount of metals exhibiting catalytic actions, especially of iron contained in it. T. H. P.

**Effect of Lime on the Insoluble Phosphates in the Soil.** By WALTER F. SUTHERST (*Chem. News*, 1902, 85, 157).—When ferrous, ferric, and aluminium phosphates containing respectively 25·92, 23·26, and 28·68 per cent. of phosphoric acid were digested in quantities of a gram each with 1 gram of citric acid dissolved in 100 c.c. of water, for 24 hours, 10·64, 10·62, and 11·16 per cent. of the total phosphoric acid in each case passed into solution. By digesting 1 gram of each of these phosphates, however, with 2 grams of lime in 100 c.c. of water for periods of 24, 48, and 72 hours, neutralising the lime with citric acid, and then subjecting the products to the treatment with citric acid, the quantity of phosphate dissolved was in all cases greatly augmented, and after the 72 hours' digestion with lime amounted to 85·88, 96·55, and 72·00 per cent. of the total phosphoric acid in the ferrous, ferric, and aluminium phosphates respectively. D. A. L.

**Origin of Arsenic in Certain Beers.** By ARTHUR PETERMANN (*Bul. Inst. Chim. Bact. de l'Etat Gembloux*, 1902, No. 72, 18—21).—The examination of five samples of Belgian superphosphate showed that two of them contained traces of arsenic, whilst the rest contained 0·017 to 0·136 per cent. It is estimated that the most impure of the above superphosphates, when applied at the rate of 1000 kilos. per hectare, would only furnish 0·000068 per cent. of arsenious acid in 20 cm. of soil, and, according to Sorauer, less than 0·1 per cent. of arsenious acid in the soil is harmless.

More than twenty samples of barley, malt, and beer from soil manured with superphosphate (in one case, 5000 kilos. had been applied in 12 years) were tested for arsenic. Two samples of malt showed a feeble reaction, whilst the other samples gave negative results.

The conclusion is drawn that, although superphosphate generally contains arsenic, barley manured with arsenical superphosphate does not contain more than traces, if any. The presence of appreciable amounts of arsenic in beer must therefore be due to impure glucose.

N. H. J. M.

**Value of Peat Ash as Manure.** By JOHANNES BOES (*Zeit. öffentl. Chem.*, 1902, 8, 150—151).—A sample of peat from the neighbourhood of Potsdam was found to contain 12·84 per cent. of ash of the following average composition :

K <sub>2</sub> O.	Na <sub>2</sub> O.	CaO.	MgO.	Fe <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .
0·6	0·5	40·9	0·47	4·6	1·05	4·1

N. H. J. M.

## Analytical Chemistry.

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**Gravimetric Estimation of Hydrogen Peroxide.** By GEORGE E. HOSCH (*J. Amer. Chem. Soc.*, 1902, 24, 479. Compare this vol., ii, 222).—Five c.c. of the sample are decomposed in a modified Schrötter's carbonic acid apparatus by means of a saturated solution of lead acetate; the loss in weight represents the oxygen evolved from the hydrogen peroxide alone. If the samples are acid, a weak soda solution should be employed as is done when effecting the decomposition by means of calcium hypochlorite. L. DE K.

**Volumetric Estimation of Iodides in presence of Chlorides and Bromides.** By VICTOR THOMAS (*Compt. rend.*, 1902, 134, 1141—1143).—When an excess of thallic chloride is mixed with an alkali iodide, the whole of the iodine is liberated and thallic chloride remains in solution. The iodine is expelled by boiling and the quantity of thallic salt remaining unchanged can be determined by the method previously described (this vol., ii, 357) and if the quantity originally present is known, the amount of iodine in the alkali iodide is readily calculated. The method is applicable in presence of chlorides and bromides, but in the latter case it is advisable to expel the iodine by means of a current of air, since if the liquid is boiled some bromine may be liberated. The thallic salt used in these determinations is readily recovered by converting it into thallic chloride by the action of hydrochloric acid and potassium chlorate. C. H. B.

[**Estimation of Sulphurous Acid in Dried Fruits.**] By ADOLF BETHIEN and PAUL BOHRISCH (*Zeit. Nahr. Genussm.*, 1902, 5, 401—409).—The amounts of sulphurous acid were estimated in various samples of dried fruits, the figures found being calculated into crystallised sodium sulphite ( $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ ): Californian apricots, from 0.2162 to 1.1585; Californian peaches, 0.9921; Californian pears, 0.2399; Italian prunes, 0.2367; and "Görtzer" pears, 0.2901 per cent. The dried apples and plums analysed were found to be free from sulphurous acid. The method of estimating the latter consisted in distilling in a current of carbon dioxide, after acidifying with phosphoric acid, oxidising the distillate by means of iodine, and precipitating the resulting sulphuric acid with barium chloride as usual. It was found that about one-half of the sulphite was removed from the fruits by cooking and a little more than half by soaking over-night and then cooking. W. P. S.

**Action of Sulphites on Nitroprussides.** By JUAN FAGES (*Compt. rend.*, 1902, 134, 1143—1145).—In the well-known test for sulphites, the production of the red coloration is due to the action of zinc nitroprusside on the sulphite. The product is decomposed by acids or alkalis and is stable only in presence of an excess of sulphite. Other insoluble nitroprussides behave in the same way

as the zinc salt. Potassium ferrocyanide, which is added to increase the sensitiveness of the test, acts somewhat irregularly and seems to be beneficial chiefly because it precipitates and concentrates the red product. In presence of an excess of nitroprusside, the influence of the ferrocyanide is less marked. It can be replaced by sodium carbonate (not in excess) or any other salt which precipitates zinc without acting on the sulphite or nitroprusside or affecting the neutrality of the solution.

C. H. B.

**Estimation of Nitrous Acid in Sodium Nitrite.** By G. SCHULTZ (*Chem. Centr.*, 1902, i, 949; from *Zeit. Farben-Textil Chem.*, 1902, 1, 37—39, 149).—The accuracy of the author's process of estimating nitrous acid by means of sodium sulphanilate, which has been unfavourably criticised by Lunge, has lately been confirmed by several chemists, including Vaubel.

L. DE K.

**Rapid Estimation of Phosphorus.** By KARL RAMORINO (*Chem. Centr.*, 1902, i, 1131—1132; from *Stahl u. Eisen*, 22, 386).—A modification of Wdowiszewski's method (*Abstr.*, 1898, ii, 454). The yellow molybdate precipitate is dissolved in 10 c.c. of approximately  $N/5$  sodium hydroxide which has been standardised with ammonium phosphomolybdate dried at  $100^{\circ}$ , and the excess of alkali is then titrated with nitric acid of corresponding strength, using phenolphthalein as indicator.

L. DE K.

**Free Acid in Superphosphate.** By JULIUS OSTERSETZER (*Chem. News*, 1902, 85, 195—196).—When titrating superphosphates with  $N/2$  or  $N/10$  sodium hydroxide, some dibasic calcium phosphate forms, and with suitable indicators intermediate tints can be observed between the stage of opalescence and that of neutrality; moreover, by the use of methyl-orange, phenolphthalein, and blue- $C_4B$ , different degrees of acidity are indicated, corresponding with the formation of mono-, di-, and tri-basic phosphates. Under some conditions, phosphoric acid appears to enter into loose combination with monobasic calcium phosphate; this is the case when the acid, in the proportion of a double molecule, is allowed to act on a quantity of the phosphate corresponding with six molecules at the ordinary temperature, or to three molecules at  $100^{\circ}$ . When tricalcium phosphate is treated with phosphoric acid in excess of the quantity required to form the monobasic phosphate, part of this excess would enter into the loose state of combination and part of it would be free; it is proposed to determine the latter by an intermediate tint with alizarinsulphonic acid, which would be observed near the point of opalescence.

D. A. L.

**Iodoeosin as Indicator in Volumetric Analysis.** By CARL GLÜCKSMANN (*Chem. Centr.*, 1902, i, 1131; from *Zeit. Oesterr. Apoth. Ver.*, 40, 390—393, Part I).—Iodoeosin is quite indifferent towards boric acid, so the amount of alkali in borax, or mixtures of it with boric acid, may be sharply titrated by means of standard hydrochloric acid, using iodoeosin as indicator. Orthophosphoric acid, when titrated with standard sodium hydroxide, behaves like a monobasic acid; barium

hydroxide cannot be employed. In titrating with this indicator, a little ether should be added to the solution. L. DE K.

**Determination of Silicon in Ferro-silicon.** By GEORGE L. NORRIS (*J. Soc. Chem. Ind.*, 1902, 21, 537).—Half a gram of the powdered ferro-silicon is dissolved in a solution of 10 grams of ferric chloride, 50 c.c. of concentrated hydrochloric acid, and about 0.5 gram of tartaric acid. A gentle heat may be applied. When the solution is completed, 25 c.c. of concentrated hydrochloric acid are added, the solution is boiled, diluted with cold water, and filtered. The residue is washed with hot dilute hydrochloric acid, then with hot water, dried, ignited, and weighed. W. P. S.

**Automatic Regulation of the Evolution of Carbon Dioxide or Nitrogen in Combustions.** By IVO DEIGLMAYR (*Ber.*, 1902, 35, 1978—1982).—A capillary and T-piece are inserted between the drying tube and the potash bulbs; the former prevents the gas passing through too rapidly. The copper oxide is heated in the usual way, but the part of the tube containing the substance mixed with copper oxide is heated by burners which are supplied from a separate tap. As soon as any pressure accumulates in the rear of the capillary, the gas supply to these burners is automatically reduced or cut off by a mercury valve connected with the T-piece. With this arrangement, it is stated that the combustion regulates itself, and that the operator need only be present when it is required to turn on the supply of oxygen or air. T. M. L.

**Estimation of Potassium in Beets, Oats, Potatoes, and Ash of Plants.** By A. BOES (*Chem. Centr.*, 1902, i, 1026; from *Apoth. Zeit.*, 17, 201).—Eight grams (or less) of the material are burnt, the char is exhausted with hydrochloric acid, silica is separated as usual, also matters precipitable by barium hydroxide. After removal of the excess of barium by ammonium carbonate, the alkali chlorides are obtained by evaporation and ignition, and the potassium is then estimated as usual by means of platonic chloride. L. DE K.

**The Indirect Estimation of Alkalis in Waters.** By WALTER W. FISHER (*Analyst*, 1902, 27, 137—139).—The difference between the molecular totals of the acids and of the bases, other than potash and soda, gives a close approximation to the molecular amount of alkali present in the water. The molecular proportions of the several acids and bases are first obtained by dividing the quantities of each by their molecular weights. On multiplying the amount of alkali so found by 62, the actual weight of sodium oxide is obtained. W. P. S.

**Analyses required for Electrical Alkali Works.** By J. H. JAMES and J. C. RITCHEY (*J. Amer. Chem. Soc.*, 1902, 24, 469—475).—Directions are given for the testing of limestone, slaked lime, salt, water, caustic liquor, spent brine, chlorine gas, caustic soda, and bleaching powder. L. DE K.

**Volumetric Estimation of Zinc: a New Indicator.** By EUGÈNE PROTHIERE (*J. Pharm. Chim.*, 1902, [vi], 15, 419—422).—In the volumetric estimation of zinc by means of sodium sulphide, it has been customary to use lead acetate as indicator. As this salt, however, undergoes double decomposition with zinc sulphide, the estimation is not sharp. The author therefore recommends the use of antimony, in the form of tartar emetic, as indicator, whereby very sharp titrations are obtained.

A. F.

**Electrolytic Deposition of Lead from a Phosphoric Acid Solution.** By ALVIN F. LINN (*J. Amer. Chem. Soc.*, 1902, 24, 435—439).—The lead solution, which should not contain more than 0.1 gram of the metal, is mixed with 10 c.c. of a solution of sodium hydrogen phosphate and the precipitate is dissolved by adding 12—14 c.c. of phosphoric acid of sp. gr. 1.71. After diluting to 130 c.c., the metal may be completely deposited by electrolysis in 12—14 hours, using a current having  $ND\ 3_{100} = 0.003$  ampere and voltage 3.

Although manganese by itself is not precipitated under these conditions, it seems to partially deposit in the presence of lead.

L. DE K.

**Estimation of Copper by Aluminium Foil.** By GEORGE E. PERKINS (*J. Amer. Chem. Soc.*, 1902, 24, 478).—The nitric acid solution of the copper ore is evaporated with large excess of sulphuric acid until dense white fumes appear. After diluting the residue with five times its bulk of water, the liquid is boiled with a few pieces of sheet aluminium, which rapidly precipitates the copper as metal; this may then be washed with water, finally with alcohol, and collected on a tared Gooch asbestos filter.

L. DE K.

**Toxicological Detection of Mercury.** By DIOSCORIDE VITALI (*Chem. Centr.*, 1902, i, 1075; from *Boll. Chim. Farm.*, 41, 149—153).—The author states that on boiling the black precipitate produced by hydrogen sulphide (when applying Fresenius and Babo's process) with nitric acid, a white substance was obtained, which, on closer investigation, proved to be the compound of mercuric nitrate with mercuric sulphide described by Rose and Barfoed. It is therefore advisable to test any such white precipitate, not only for lead, but also for mercury.

L. DE K.

**Volumetric Estimation of Mercury and also of Silver and Mercury.** By ERWIN RUPP and LUDWIG KRAUSS (*Ber.*, 1902, 35, 2015—2017. Compare R. Cohn, this vol., ii, 50).—Cohn's method, titration of mercury salts by the aid of ammonium thiocyanate in the presence of iron alum, yields good results when excess of nitric acid is present. The method is not applicable for the estimation of mercuric chloride. For the estimation of silver and mercury in the same solution, the sum of the two is first determined by the above method and then the silver estimated separately by the Gay-Lussac shaking method with  $N/10$  sodium chloride.

J. J. S.

**Colorimetric Estimation of Mercury in Urine.** By FRIEDRICH ESCHBAUM (*Chem. Centr.*, 1902, i, 1133—1134; from *Pharm. Zeit.*, 47, 260—261. Compare Abstr., 1900, ii, 368).—The method is intended for the estimation of quantities of mercury so small as to be scarcely weighable. The copper gauze containing the mercury obtained in the usual way from 200—2000 c.c. of urine is well washed with alcohol and ether and dried for half-an-hour in the air. It is then heated in a loosely corked tube so as to sublime the mercury. The tube is then divided into two parts by the usual blow-pipe manipulation. The tube containing the mercurial deposit is placed in hot water and rinsed a few times with 1—2 c.c. of chlorine water. The solution is evaporated to about 0.5 c.c., filtered into a tube having a mark at 1 c.c., and the dish and filter are then rinsed with a few drops of water. One drop of solution of stannous chloride is added, and the turbidity thus produced is compared with that of a very weak solution of mercuric chloride of known strength treated with stannous chloride in the same manner. L. DE K.

**Volumetric Estimation of Alumina and of Free and Combined Sulphuric Acid in Alums.** By ALFRED H. WHITE (*J. Amer. Chem. Soc.*, 1902, 24, 457—466).—Three grams of commercial alum are dissolved in 100 c.c. of water. To 25 c.c. of this are added 50 c.c. of a neutral 10 per cent. solution of potassium sodium tartrate, and the liquid is titrated with  $N/5$  barium hydroxide, using phenolphthalein as indicator. The result represents the sum of the alumina and combined and free sulphuric acid. Another 25 c.c. are evaporated to dryness on the water-bath, and the residue, after being redissolved in 50 c.c. of a neutral 10 per cent. solution of sodium citrate, is again titrated. The difference between the two titrations is equivalent to one-third of the sulphuric acid combined with aluminium, and, consequently, to one-third of the aluminium present. In this process, the precipitation of barium sulphate is retarded for a considerable time. L. DE K.

**Modification of Rose's Method of Separating Cobalt and Nickel.** By ROBERT L. TAYLOR (*Proc. Man. Phil. Soc.*, 1902, 46, No. 11, 1—7).—Rose's original process, as is well known, consists in saturating the dilute solution of the two metals, which should contain free hydrochloric acid, with chlorine, and precipitating the cobalt as sesquioxide by adding an excess of barium carbonate. The precipitation is, however, very slow, and this, according to the author, is caused by the presence of the liberated carbon dioxide.

The modification now proposed is as follows: the liquid containing the cobalt and nickel is freed from excess of acid by evaporation, or, more conveniently, by boiling for a short time with an excess of barium carbonate, and when cold an excess of bromine water is added. After 10 minutes, the cobalt has separated quantitatively as sesquioxide. The method is equally useful in qualitative work. L. DE K.

**Estimation of Titanium.** By GEORGE B. WATERHOUSE (*Chem. News*, 1902, 85, 198—199).—To estimate titanium gravimetrically in

steels or pig-irons, 5 grams of drillings are dissolved by warming with 50 c.c. of strong hydrochloric acid, and the solution is boiled, evaporated to dryness, and well baked. It is then treated with 20 c.c. of hydrochloric acid, heated, and the iron chloride removed by boiling with 70 c.c. of water, washing with warm 1:1-hydrochloric acid, and with cold water. The solution is made up to 150 c.c. with water, neutralised with dilute ammonia, any precipitate dissolved by a few drops of hydrochloric acid, and the whole reduced by slowly treating with 50 c.c. of a 1:5 solution of sodium sulphite with the aid, if necessary, of a little dilute sulphuric acid. The reduced solution is mixed at the boiling point with 50 c.c. of glacial acetic acid, and with a hot, filtered solution containing 20 grams of sodium acetate, boiled briskly for 15 minutes, and filtered. The precipitate, along with the residue from the first treatment with hydrochloric acid and water, is dried, ignited, and fused with 10 grams of sodium carbonate; the mass, when cold, is digested with 150 c.c. of hot water, and the washed residue boiled briskly with 10 c.c. of dilute sulphuric acid until heavy fumes are evolved; when cool, 50 c.c. of water are added, the solution filtered, made up to 150 c.c., and dilute ammonia added until a faint precipitate is permanently formed. This is redissolved as before and the treatment with sodium sulphite repeated, using 20 c.c.; the reduced solution is heated to boiling, mixed with sodium acetate and acetic acid as before, boiled for 15 minutes, and the precipitate washed, dried, ignited, and weighed as titanous oxide. The method has proved satisfactory in the presence of chromium, aluminium, nickel, tungsten, molybdenum, and vanadium.

D. A. L.

**Electrolytic Estimation of Vanadium.** By P. TRUCHOT (*Ann. Chim. anal.*, 1902, 7, 165—167).—The compound containing about 0.012—0.05 gram of vanadium pentoxide is fused with sodium carbonate, the mass is dissolved in cold water, very slightly acidified with dilute sulphuric acid, boiled to expel carbon dioxide, diluted to 200 c.c., and rendered alkaline with 20—30 drops of ammonia. After heating to 85—90°, the liquid is submitted for 8—10 hours to electrolysis, using at first a current of 2.5 volts and 0.15 ampere, and towards the end one of 0.3 ampere. Care should be taken that the alkaline reaction of the liquid is maintained during the electrolysis. The vanadium is deposited on a weighed platinum cathode of about 80 decimetres square as hydrated oxide, which is afterwards converted into pentoxide by ignition in a muffle. After cooling in a desiccator, it must be quickly weighed as it is very hygroscopic.

L. DE K.

**Detection of Traces of Vanadium and its Separation from Molybdenum.** By P. TRUCHOT (*Ann. Chim. anal.*, 1902, 7, 167—168).—The smallest amount of vanadium electrolytically deposited on platinum (compare preceding abstract) may be identified by heating the spot with a pinch of potassium hydrogen sulphate and then dissolving in a few drops of sulphuric acid, when a yellow solution will be obtained. If now a few crystals of strychnine sulphate are added, a bluish-violet coloration is obtained which turns to a bright rose. The action of some other alkaloids and phenols is as follows: atropine,



caffeine, and santonin, no effect; phenol gives a dark green, and pyrogallol a brownish-black colour.

*Separation of Vanadium from Molybdenum.*—The author states that molybdenum forms a deposit on platinum similar to that of vanadium, but it may be completely volatilised by heating to redness for about half-an-hour.

L. DE K.

*Analysis of an Alloy containing Antimony, Tin, and Copper, also Iron and Lead.* By PONTIO (*Ann. Chim. anal.*, 1902, 7, 163—164).—Five grams of the alloy are dissolved in excess of hydrochloric acid and a few drops of strong nitric acid and diluted with water to 1 litre. (If on adding the water the liquid becomes turbid, more hydrochloric acid should be added.) One hundred c.c. of the solution are evaporated to about 5 c.c. and then boiled for 20—25 minutes with addition of 50 c.c. of fuming nitric acid and a few grams of potassium chlorate, which causes the oxides of antimony and tin to precipitate. After adding an equal bulk of water, the cold liquid is filtered, the oxides are washed with hot water acidified with nitric acid, dried, ignited, and weighed. They are then digested with 50 c.c. of dilute hydrochloric acid (3:1) and a strip of pure tin. When the tin has dissolved, the metallic antimony is collected on a tared filter, washed first with boiling water, then with alcohol, dried at 110°, and weighed. Its weight multiplied by 1.26 represents the antimony tetroxide contained in the mixed oxides; the difference consists of tin dioxide which is then calculated into tin.

The filtrate from the tin and antimony oxides is evaporated to dryness, the residue boiled with dilute hydrochloric acid and (after neutralisation) mixed with excess of hot concentrated solution of sodium sulphide; the sulphides are washed with dilute sodium sulphide, redissolved in nitric acid, and evaporated with sulphuric acid. The lead sulphate is collected as usual and weighed. The filtrate containing the copper and iron is concentrated by evaporation and the copper determined electrolytically, using a current of 2 volts and 0.5 ampere. The iron is then estimated in the filtrate by precipitation with ammonia. In default of electrical appliances, the iron may also be separated from the copper by repeated precipitation with ammonia. The ammoniacal solution is then acidified with hydrochloric acid, the copper precipitated with pure zinc, and then converted by ignition into oxide.

L. DE K.

*Electrolytic Determination of Bismuth.* By OTTO BRUNCK (*Ber.*, 1902, 35, 1871—1873).—Bismuth is precipitated quantitatively and in a compact form on a wire gauze electrode provided that the current density does not exceed 0.5 ampere per 100 sq. cm. for a solution containing 0.1 gram of bismuth per 100 c.c., or 0.1 ampere per 100 sq. cm. for a solution containing 0.05 gram per 100 c.c. The best method is to dissolve the metal or compound in enough nitric acid to prevent the separation of basic salts on diluting to 100 c.c., to electrolyse with an *E.M.F.* of only 2 volts from a battery of accumulators in parallel, and to start the electrolysis at 70—80°, allowing the solution to cool gradually so as automatically to reduce current-density

as the solution becomes more dilute. The method does not suffice to separate bismuth and lead, for the lead peroxide which separates at the anode always contains bismuth. The maximum error recorded for solutions of pure bismuth is 0.0005 gram on 0.01 gram of bismuth.

T. M. L.

**Iodometric Estimation of Gold.** By ERWIN RUPP and SPIESS (*Ber.*, 1902, 35, 2011—2015).—The method is based on the reduction of gold chloride by arsenious oxide according to the equation  $3\text{As}_2\text{O}_3 + 4\text{AuCl}_3 + 6\text{H}_2\text{O} = 3\text{As}_2\text{O}_5 + 12\text{HCl} + 4\text{Au}$ . A hydrochloric acid solution of auric chloride free from nitric acid is mixed with an excess of *N*/10 arsenious oxide solution and warmed on the water-bath until quite clear. Excess of sodium hydrogen carbonate is added and the unaltered arsenious oxide titrated with standard iodine solution. Alkalis, ammonia, and alkali carbonates must not be present in the gold solution.

It is stated that the Gooch-Morley direct method of titration (*Abstr.*, 1900, ii, 110) gives too high results, probably due to the spontaneous reduction of the aurous iodide and the liberation of a further quantity of iodine.

J. J. S.

**Application of the  $\beta$ -Naphthylhydrazones to the Detection and Separation of the Sugars.** By ALBERT HILGER and S. ROTHENFUSSER (*Ber.*, 1902, 35, 1841—1845).—Galactose  $\beta$ -naphthylhydrazone, best prepared by adding a concentrated aqueous solution of the sugar to an alcoholic solution of the hydrazine, melts at 189—190° and has the solubility 0.0932 per cent. in 96 per cent. alcohol. Dextrose- $\beta$ -naphthylhydrazone melts at 178—179° and has the solubility 0.896 in 96 per cent. alcohol. Arabinose- $\beta$ -naphthylhydrazone melts at 176—177° and has the solubility 0.1816 in 96 per cent. alcohol. The physical data differ from those ascribed to the same compounds by Lobry de Bruyn and Alberda van Ekenstein (*Abstr.*, 1896, i, 588), who prepared their compounds in aqueous solution but probably did not obtain them pure, this solvent being unsuitable. To separate a mixture of the three sugars, the arabinose is first removed as the phenylbenzylhydrazone; the excess of the phenylbenzylhydrazine is removed by addition of formaldehyde and the excess of the latter by evaporation. In the filtrate, the galactose may be precipitated by  $\beta$ -naphthylhydrazone, the excess of which is then removed by formaldehyde. Finally, the dextrose may be precipitated by diphenylhydrazine. The galactose may also be removed before the arabinose. The extraction of the formaldehyde- $\beta$ -naphthylhydrazone from the filtrate containing dextrose must be effected with ethyl acetate, ether being unsuitable.

A. H.

**Analysis and Testing of Kiln-dried Malt.** By EUGEN PRIOR (*Zeit. angew. Chem.*, 1902, 15, 455—462).—It is recommended that the scheme of the analysis of malt should include the following items; no novel analytical processes are given or required.

Colour of the 10 per cent. solution expressed in *N*/100 iodine; number of minutes required for saccharification. *Calculated on dry substance.*—Amount of diastase, extract, total invertable substances

(expressed as starch), pre-existing inverted substances (expressed as starch), total maltose, maltose in 100 parts of extract, maltose in the pre-existing inverted substances, total dextrin value, dextrin in the pre-existing inverted substances, starch inverted by diastase, maltose formed by diastase, dextrin formed by diastase, diastase present for 100 parts of starch, amount of starch inverted, and amount of maltose and dextrin formed by the action of 1 gram of diastase, amount of starch inverted by 1 gram of diastase in 10 minutes, relation between 1 part of total dextrin and maltose, relation between 1 part of dextrin produced by diastase and maltose, lactic acid, and appearance of the wort.

The physical properties include weight per hectolitre, amount of glassy grains, hard grains, brown grains, and white, mealy grains. Analyses of 20 different malts are communicated in a table.

L. DE K.

**A Sensitive Test for the Detection of Formaldehyde.** By CARL ARNOLD and CURT MENTZEL (*Zeit. Nahr. Genussm.*, 1902, 5, 353—356).—To detect the presence of formaldehyde in meat, butter, or milk, from 5 to 10 grams of these articles of food are extracted with 10 c.c. of absolute alcohol. After filtering, 5 c.c. of the alcoholic filtrate are mixed in a test-tube with 0.03 gram of phenylhydrazine hydrochloride, 4 drops of ferric chloride solution, and 10 drops of concentrated sulphuric acid. The solution is kept cool during the addition of the latter. Should formaldehyde be present, the solution is coloured red, whilst in the absence of this preservative it remains yellow. The test is applicable directly to light coloured beers. In the case of dark beers, the coloration may be observed in the froth produced on shaking the contents of the test-tube, or the red-colouring matter may be extracted with ether, and the latter evaporated. On adding alcohol and sulphuric acid to the residue, the red coloration re-appears. The sensitiveness of the test is about 1:10,000.

W. P. S.

**Estimation of Tartaric Acid in Grape Marc.** By C. EHRMANN and H. LOVAT (*Chem. Centr.*, 1902, i, 1028; from *Oesterr. Chem. Zeit.*, 5, 121—124).—One hundred grams of the comminuted material are mixed in a counterpoised flask with 20 c.c. of hydrochloric acid of sp. gr. 1.1, and the weight of the liquid is then increased by dilution with water to 950 grams. After heating in a boiling water bath for 1½ hours, the loss by evaporation is restored and the liquid is filtered. Five hundred c.c. of the filtrate are evaporated in a porcelain dish to 100 c.c., mixed with 35 c.c. of a 20 per cent. solution of potassium carbonate, and boiled for some time. When cold, the liquid is diluted to 200 c.c. and filtered, and 100 c.c. are then evaporated to 15 c.c. While still hot, the dish is covered with a watch glass and 3 c.c. of glacial acetic acid are introduced. The further details are those of the process communicated by Goldenberg, Géromont and Co. (*Abstr.*, 1898, ii, 465, 545). In calculating the result of the titration, it is assumed that the marc contains 50 per cent. of water, if, however, this is not the case, a slight correction should be made.

Efforts are being made to use the Halenke-Möslinger process for

the estimation of total tartaric acid, but the experiments have not yet been concluded.

L. DE K.

**Estimation of Total Tartaric Acid in Lees and Tartars.** By A. HUBERT (*Ann. Chim. anal.*, 1902, 7, 168—174).—A modification of the Goldenberg method, in which the lees or the tartars are dissolved in dilute hydrochloric acid (1 : 3), boiled with excess of potassium carbonate, and precipitated with acetic acid and excess of alcohol. The potassium hydrogen tartrate, after being washed with alcohol, is finally titrated with  $N/2$  sodium hydroxide, using phenolphthalein as indicator.

In order to obtain accurate results, a correction is necessary. Starting from 6 grams of material and 200 c.c. of dilute acid, using a plaited filter of 10 cm. in diameter and carefully measuring the filtrate, 50 c.c. of which are used for the estimation, the true percentage of tartaric acid will be obtained by means of the formula  $[A + (200 - A)/2]/200 \times B$ , in which  $A$  is the volume of the filtrate plus 1 c.c. and  $B$  the percentage of tartaric acid as found by titration.

Drawings are given of suitable shaking apparatus when dissolving the samples in dilute hydrochloric acid. An apparatus is also described in which the hydrochloric acid solution of the sample is precipitated with a solution of calcium acetate. The height of the column of calcium tartrate then indicates at once the percentage of tartaric acid.

L. DE K.

**Test for the Gumming Quality of Lubricating Oils.** By AUGUSTUS H. GILL (*J. Amer. Chem. Soc.*, 1902, 24, 467—468).—The author employs the elaidin test for judging the quality of lubricating oils. Five grams of the sample are stirred with 11 grams of nitrosulphuric acid (prepared by saturating sulphuric acid of sp. gr. 1.47 containing a few drops of nitric acid with nitric oxide at 0°). In the case of bad oils, brown masses form around the edges and become red in a few hours. The quality of the oils may also be judged by the amount of oxygen absorbed on heating. This is determined by heating the sample in a sealed tube for at least 100 hours and then breaking the point under water. The volume of water entering the tube represents the volume of the oxygen absorbed. Several results are given in a table.

L. DE K.

**Analytical Constants of Neatsfoot, Tallow, and Horse Oils.** By AUGUSTUS H. GILL and ALLAN W. ROWE (*J. Amer. Chem. Soc.*, 1902, 24, 466—467).—Tables giving the results of the testing of five samples of neatsfoot oil, three of tallow oil, and five of horse oil, all supposed to be genuine.

The examination included sp. gr. at 15°, Valenta test using 100 per cent. acetic acid, Maumené test using 100 per cent. sulphuric acid, specific temperature reaction, iodine number (4 hours' action), Lewkowsch titre test and iodine number of the fatty acids.

The figures obtained with the neatsfoot oils are fairly, and those with the tallow oils remarkably, concordant, but those with the horse oils show considerable variation, the Valenta test being here of no use whatsoever.

L. DE K.

**Metallic Soaps from Linseed Oil and their Solubility in certain Hydrocarbons.** By HERMANN T. VULTÉ and HARRIET W. GIBSON (*J. Amer. Chem. Soc.*, 1902, **24**, 215—222).—Starting with the sodium soap from pure linseed oil, the authors have prepared by double decomposition the soaps of lead, mercury (mercuric), copper, tin (? stannous), antimony, iron (ferrous), chromium, aluminium, nickel, cobalt, manganese, zinc, barium, and calcium, and investigated the solubility of these compounds after 1, 24, and 48 hours' immersion in the following solvents: light petroleum, sp. gr. 0.639, b. p. 35—55°; ditto, sp. gr. 0.702, b. p. 55—75°; ditto, sp. gr. 0.695, b. p. 75—85°; ditto, sp. gr. 0.698, b. p. 71°; naphtha, sp. gr. 0.741, b. p. 59°; ditto, sp. gr. 0.732, b. p. 62°; gasoline, sp. gr. 0.699, b. p. 74°; turpentine, sp. gr. 0.855. From the results which have been duly tabulated it will be seen that lead soap deposits almost completely within an hour from its solution in any of the petroleum solvents; nickel soap, although nearly completely separating in time, remains in solution for several days; iron soap is permanently soluble and an excellent drier, whilst manganese soap is unsurpassed in its drying properties.

So far as it has been carried, the investigation discloses the following facts: (1) The percentage of separation of the metallic soaps of linseed oil in the hydrocarbon solvents differs with the nature of the solvent and the linoleate. (2) Each soap affords a maximum percentage of solubility in some special hydrocarbon, and therefore no general solvent can be used for all metals. (3) The time at which the maximum separation takes place varies with the metal employed. L. DE K.

**The Bechi Test for Cottonseed Oil.** By AUGUSTUS H. GILL and CHARLES H. DENNISON (*J. Amer. Chem. Soc.*, 1902, **24**, 397—398).—The evidence obtained by the authors tends to show that the coloration produced by some oils with the Bechi test is due to a sulphur compound in the oil itself. In view of the fact that substances of an aldehydic character could not be detected in the oil either by the magenta aldehyde reagent, by sodium hydrogen sulphite, or by ammonia, it is not likely that they are present. In two instances, however, the black compound formed in the test gave off hydrogen sulphide.

W. P. S.

**Detection of Sesamé Oil in Chocolate.** By FRANZ UTZ (*Chem. Zeit.*, 1902, **26**, 309).—Attention is called to the fact that the active principle of sesamé oil suffers decomposition on heating, and that it is therefore of great importance not to submit the ethereal extract of the chocolate to prolonged heating or to too high a temperature (compare Posetto, *Abstr.*, 1901, ii, 703).

The author prefers Soltsien's stannous chloride reaction to Baudouin's hydrochloric acid sugar test.

L. DE K.

**Application of Gerber's Method of Fat Estimation to Sheep's Milk.** By C. BEGER and H. WOLFS (*Chem. Zeit.*, 1902, **26**, 309).—As the result of 61 experiments, it is stated that the fat in sheep's milk may be estimated with great accuracy by using Gerber's apparatus, which has found such a wide application in ordinary milk analysis.

L. DE K.

**Micro-chemical Detection of Alkaloids.** By M. EMM. POZZI-ESCOT (*Ann. Chim. anal.*, 1902, 7, 125. Compare Abstr., 1901, ii, 432, 485).—In reply to many inquiries, the author still adheres to his opinion that the micro-chemical detection of alkaloids cannot, as yet be trusted in serious investigations.  
L. DE K.

**Estimation of Alkaloids in Kola Nut and its Fluid Extracts.** By J. WARIN (*J. Pharm. Chim.*, 1902, [vi], 15, 373—377).—The residue obtained by the evaporation of the alcohol from 15 grams of the fluid extract to be analysed are triturated with 10 grams of calcined magnesia and 2 grams of water. After leaving the mixture for some time, it is placed in a dry flask, together with 150 c.c. of chloroform, and the mixture boiled under a reflux condenser for 3/4 hour. The flask must be weighed before and after heating, and any loss of chloroform must be made good by a corresponding addition of this liquid. The chloroform solution is now filtered, and the residue left by evaporation of a known volume is weighed. This gives the amount of crude alkaloid present, and if greater accuracy is desired the crude residue must be purified by solution in hydrochloric acid and subsequent solution in chloroform after precipitation with ammonia.

In the case of kola nut, 15 grams of the powder are triturated with 10 grams of calcined magnesia and 15 c.c. of water, and the estimation then carried out as above.  
H. R. LE S.

**Detection of Aloin, Tyrosine, Logenin, Opium Preparations, Tincture of Cachou.** By ÉMILE BOURQUELOT (*J. Pharm. Chim.*, 1902, [vi], 15, 342—345. Compare Abstr., 1900, i, 512; ii, 583).—If to a solution of commercial aloin a few drops of a mixture of 1 part *Russula delica* extract and 2 parts of glycerol be added, a purple-red coloration is produced. If, however, the isobarbaloin be removed from the commercial aloin by recrystallisation, then no such colour reaction takes place.

Hirschsohn's test (*Pharm. Centralhalle*, 42, 63) is very suitable for the detection of tyrosine.

This paper also contains modifications of the tests employed for the detection of logenin, opium preparations, and tincture of cachou, for the details of which the original communication must be consulted.

H. R. LE S.

**Note on Reichard's "Silver" Method for the Estimation of Morphine in Opium.** By PHILIP SCHIDROWITZ (*Analyst*, 1902, 27, 117—118).—The results of the experiments described in this paper show that the quantity of silver reduced in the estimation of morphine by Reichard's process (see Abstr., 1901, ii, 707) is largely dependent on the quantity of silver solution employed. In its present form, the method must be regarded as useless.  
W. P. S.

**Estimation of Essence of Mustard.** By P. ROESER (*J. Pharm. Chim.*, 1902, [vi], 15, 361—364).—The methods used for the estimation of essence of mustard in natural or artificial essential oils are based on the formation of silver sulphide by the action of an ammoniacal

solution of silver nitrate on thiosinamine, which last is readily produced by the action of ammonia on the mustard oil. The following method is based on Denigès's cyanide method for the estimation of silver. Five c.c. of a 1 per cent. solution of the mustard oil in alcohol (95°) are mixed with 10 c.c. of ammonia solution and 10 c.c. of *N*/10 silver nitrate and the mixture repeatedly shaken. After 24 hours, the mixture is diluted to 100 c.c., filtered, and 5 c.c. of *N*/10 potassium cyanide added to 50 c.c. of the filtrate. The excess of potassium cyanide is then titrated with *N*/10 silver nitrate in the presence of 8 drops of a slightly ammoniacal solution of potassium iodide (1/20). If, now, the number of c.c. of silver nitrate actually required be multiplied by 2 and by 17, the product is the quantity of silver nitrate actually converted into silver sulphide. The last number, when multiplied by 0.7294, gives the amount of silver sulphide formed, which, when multiplied by the factor 0.4301, gives the actual amount of mustard oil present in the 5 c.c. originally taken.

H. R. LE S.

**Characterisation of Aloes and their Detection in Pharmaceutical Preparations.** By EUGÈNE LÉGER (*J. Pharm. Chim.*, 1902, [vi], 15, 335—341).—Sodium peroxide, when added to a solution of aloes maintained at 80°, produces first a brown coloration, which, as the addition of the peroxide proceeds, becomes a beautiful cherry-red. The production of this cherry-red colour is a very delicate test for the presence of aloes. If the solution to be tested is coloured by such substances as rhubarb, emodin, &c., it is necessary to remove these by means of basic lead acetate before adding the sodium peroxide.

H. R. LE S.

**Analysis of Rubber-Wares.** By FRITZ FRANK and ED. MARCKWALD (*Chem. Zeit.*, 1902, 26, 335).—A criticism of the method proposed by Heintz (this vol., ii, 369). It is stated that the admixed organic substances are difficult of extraction unless the fillings are first removed. The alkali used to extract the "factis" can only be removed by long treatment with boiling water, and the residue is difficult to dry. Objections are also raised to the method employed for the estimation of the organic hydrogen and to the factor used in the calculation; moreover, a hydrogen estimation does not suffice, but should be supplemented by a carbon determination. Volatile mineral substances also interfere with the process.

L. DE K.

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## General and Physical Chemistry.

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**Action of Light.** By ANDREA ARCHETTI (*Chem. Zeit.*, 1902, 26, 555).—Chloroform reduces Fehling's solution when the mixture is exposed to diffused light. On exposure to direct sunlight, glycerol slowly reduces mercuric chloride to mercurous chloride and finally to mercury, and ferric chloride to ferrous chloride, becoming itself converted into a substance which reduces Crismer's aldehyde reagent and dissolves ferric hydroxide in presence of excess of alkali. G. Y.

**Kinetics of Photochemical Reactions. Oxidation of Quinine by Chromic Acid.** By EMANUEL GOLDBERG (*Zeit. physikal. Chem.*, 1902, 41, 1—10).—The above reaction, which proceeds in the dark with extreme slowness, has been studied quantitatively, the extent of oxidation at any time being determined by running a certain volume of the reaction mixture into potassium iodide and titrating with sodium thiosulphate. In all the experiments, the quinine was in excess, and only the first stages of the process were studied, because of the colour changes involved. The oxidation is accelerated chiefly by the blue and violet rays,—an observation in accordance with Vogel's law that only those rays which are absorbed can be chemically active. It has been found also, in accordance with Bunsen and Roscoe's law, that the chemical action or accelerating influence of the light is proportional to its intensity. The oxidation of quinine by chromic acid is apparently a unimolecular reaction, but when the variation of the light intensity with the concentration is taken into account, it is found to be bimolecular. The author argues on various grounds that the mechanism of photochemical reactions in the light is quite distinct from what it is in the dark. Thus when the mixture of quinine and chromic acid is (1) kept hot in the dark, (2) kept cool in the light, quite different products appear to be formed in the two cases. Again, in this and other photochemical reactions, the temperature coefficient of the velocity constant is extremely small compared with that of ordinary reactions the progress of which is not affected by light. J. C. P.

**Gas Elements.** By RICHARD LORENZ (*Zeit. anorg. Chem.*, 1902, 31, 275—278).—In reply to Bose's criticism (this vol., ii, 375) of Czepinski's work on gas elements (this vol., ii, 298) the reversible nature of the oxygen | hydrogen cell is discussed. The author also discusses in more detail the four kinds of gas electrode potentials already dealt with (*Zeit. anorg. Chem.*, 1899, 20, 420). (a) At the electrode, an electromotive active gas may pass into the ionic condition; (b) an electromotive active gas may be mixed with an inactive gas at the electrode (compare Czepinski, *loc. cit.*), and in this case the action depends on the partial pressure of the active gas and permits of the construction of gas concentration elements; (c) an electromotive active gas may be mixed with an inactive gas which is, however, not



chemically indifferent; in this instance, not only the partial pressure of the active gas but also the chemical equilibrium must be taken into account; and (d) when there is a mixture of active gases at the electrode, the potential established may be termed a "mixed potential."

J. McC.

**Inversion of Zinc Sulphate. II.** By H. T. BARNES and H. L. COOKE (*J. Physical Chem.*, 1902, 6, 172—177).—The temperature of inversion of zinc sulphate determined by the electrical method (that is, in a Clark's cell), differs considerably from that obtained by solubility measurements, and the difference has been ascribed to the presence of the mercurous sulphate in the Clark cell, by which the inversion temperature is lowered. A cell was therefore constructed of H-pattern, containing zinc sulphate over a 10 per cent. zinc amalgam, and it was found that the inversion temperature was still lower than that derived from the solubility, and was almost unaffected by the addition of mercurous sulphate. The cause of the difference cannot, therefore, be ascribed to the presence of the mercurous sulphate (Abstr., 1900, ii, 254).

L. M. J.

**Electrical Resistance of Metallic Sulphides.** By JOSEPH GUINCHANT (*Compt. rend.*, 1902, 134, 1224—1225).—The author has determined the electrical resistance of previously fused metallic sulphides at various temperatures between  $-25$  and  $920^{\circ}$ . The resistance of lead sulphide between  $-25^{\circ}$  and  $100^{\circ}$  is represented by the equation  $\rho_t = 0.000928 (1 + 0.00501t)$ , and it increases with the temperature up to  $920^{\circ}$ . In the case of stannous sulphide, the resistance decreases continually with the temperature up to  $920^{\circ}$ ; between  $0^{\circ}$  and  $100^{\circ}$ , it is represented by the expression  $\rho_t = 1071 (1 - 0.00662t)$ . Ferrous sulphide behaves differently; its resistance decreases as the temperature rises, up to  $550^{\circ}$ , and then increases with the temperature until at about  $870^{\circ}$  it has the same resistance as at  $200^{\circ}$ . During cooling, the reverse changes take place, but the resistance lags somewhat behind the temperature. Between  $0^{\circ}$  and  $100^{\circ}$ , the resistance is represented by the equation  $\rho = 0.114 (1 - 0.00798t)$ . Other sulphides belong to one or other of these types, according to their conductivity. In all cases, the *rate of change* of the resistance increases with the temperature, and its value is higher the greater the resistance. With good conductors the value is always positive; with bad conductors, it is at first negative, but changes in sign when the value of the resistance has reached a certain low point. It seems probable that the sign of the coefficient of temperature depends on the magnitude of the resistance, or causes which determine it, and not on accessory phenomena such as electrolysis.

C. H. B.

**Influence of Voltage on the Formation of Ozone.** By A. CHASSY (*Compt. rend.*, 1902, 134, 1298—1300).—When a small *E.M.F.* is applied to an ozoniser, no ozone is formed, but as the *E.M.F.* is increased, ozone begins to form at a certain point and a further rise of *E.M.F.* causes a very rapid increase in the amount of ozone formed. When the *E.M.F.* is high, the power of the current to produce ozone

is proportional to the square of the potential difference which exists between the armatures. As this law is not applicable until a certain *E.M.F.* is reached (which depends on the size of the apparatus), the author introduces the idea of a dielectric inertia to explain the irregularity.

J. McC.

**Depolarisation of the Hydrogen Electrode by Compounds of the Aromatic Series.** By A. PANCHAUD DE BOTENS (*Zeit. Elektrochem.*, 1902, 8, 305—315, 332—346).—The difference of potential between a platinised platinum electrode saturated with hydrogen and a normal solution of sulphuric acid (or potassium hydroxide) containing some 10 per cent. of alcohol is diminished considerably by the addition of a reducible substance to the solution. The magnitude of the diminution is regarded as a measure of the facility of reduction of the compound used. The 53 compounds used gave the following diminutions of *P.D.* in acid solution. Nitroso-compounds 0.64—0.5 volt. Mononitro-compounds, 0.33—0.23 volt. Nitrosoamines and isodiazohydrates, 0.16—0.09 volt. Diazonium compounds, 0.47—0.37 volt. Normal diazotates do not depolarise. Of the dinitro-derivatives of benzene used, the ortho-compound gave the largest depolarisation; other similar regularities were not observed.

T. E.

**Electrocapillary Properties of Organic Bases and their Salts.** By A. GOUY (*Compt. rend.*, 1902, 134, 1305—1307. Compare Abstr., 1901, ii, 83, 435, 592; this vol., ii, 194).—Organic bases are the more active as their molecular complexity increases. Their salts, too, are active. The experiments were made by comparing the electrocapillary curve of a solution of sulphuric acid with that of the same solution after the addition of a base, and both against that of a solution of sodium sulphate containing mercurous sulphate. The active anion depresses the positive branch of the curve, whilst the active cation depresses the negative branch. The strong bases have almost the same curve as the salts, but that of weak bases is lower than that of the corresponding salts. The effect of the free base is mainly due to the undissociated part; the effect produced by the salts is to be attributed to the active cations. In general, non-electrolytes are more active than electrolytes.

J. McC.

**Conductivity of Aqueous Solutions of Electrolytes consisting of Univalent Ions.** By FRIEDRICH KOHLRAUSCH and H. VON STEINWEHR (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 581—587).—The following salts were examined: Cæsium chloride, thallous chloride, potassium iodide, potassium bromide, potassium thiocyanate, potassium fluoride, sodium fluoride, thallous fluoride, thallous nitrate, silver nitrate, and potassium chlorate. The behaviour of thallous chloride differs from that of the chlorides of the alkali metals; the equivalent conductivity increases more quickly with rising concentration above 0.001 *N*, and this is connected with the power of thallium of occurring in a polyvalent form. Thallous nitrate behaves quite normally, and at higher concentrations thallous fluoride is also quite normal. In dilute solution, however, thallous fluoride behaves anomalously, indicating that hydrolysis takes place.

The conductivity of very dilute solutions of silver nitrate between platinised plates increases with time, but solutions which are more than 0.01 *N* do not show this change of conductivity with time.

The conductivities of the salts examined are given in tables. From the results obtained, the following ionic mobilities at 18° are calculated: Li, 33.44; Na, 43.55; K, 64.67; Rb, 67.6; Cs, 68.2; NH<sub>4</sub>, 64.4; Tl, 66.00; Ag, 54.02; F, 46.64; Cl, 65.44; Br, 67.63; I, 66.40; SCN, 56.63; NO<sub>3</sub>, 61.78; ClO<sub>3</sub>, 55.03; and IO<sub>3</sub>, 33.87.

With the aid of the temperature coefficients now accurately known, the following ionic mobilities at 18° (previously only known at 25°) have been calculated: BrO<sub>3</sub>, 46.2; ClO<sub>4</sub>, 64.7; IO<sub>4</sub>, 47.7; MnO<sub>4</sub>, 53.4; CHO<sub>2</sub>, 46.7; C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, 35.0; C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>, 31.0; C<sub>4</sub>H<sub>7</sub>O<sub>2</sub>, 27.6; C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>, 25.7; and C<sub>6</sub>H<sub>11</sub>O<sub>2</sub>, 24.3. J. McC.

**Electrolysis of Aqueous Solutions with Platinised Electrodes and the Electrolytic Formation of Dithionates.** By FRITZ FOERSTER and A. FRIESSNER (*Ber.*, 1902, 35, 2515—2519).—When a solution of sulphuric acid or sodium hydroxide is electrolysed with platinised electrodes at a constant temperature and with the same strength of current, the difference of potential at the terminals and the anode potential gradually increases, whilst the difference (in volts) between the two remains constant. The cathode potential does not alter during the electrolysis, and the anode has the higher potential immediately the cathode becomes slightly polarised, showing that the phenomenon is due to small quantities of oxygen. This result is illustrated by the electrolysis of sodium sulphite. No oxygen escapes on the anode, and some SO<sub>3</sub> ions combine forming S<sub>2</sub>O<sub>6</sub> ions, whilst some combine with hydroxyl ions forming SO<sub>4</sub> ions and water. Several experiments are described, in the most successful of which 47 per cent. of the current was utilised in the formation of dithionate.

R. H. P.

**Velocity of Electrolytic Decomposition of Oxalic Acid in Presence of Sulphuric Acid.** By TEODOR AKERBERG (*Zeit. anorg. Chem.*, 1902, 31, 161—190).—When a solution of sulphuric acid containing oxalic acid is electrolysed between polished platinum electrodes, the oxalic acid is scarcely decomposed. When platinised electrodes are used, the oxalic acid is readily decomposed. The decomposition is therefore a secondary process which is catalytically influenced by the platinum black; it is a purely chemical oxidation effected by the electrolytically separated oxygen. In concentrated solution, with low current densities, or at high temperature, the decomposition follows Faraday's law, but in more dilute solution the reaction is unimolecular and consequently the oxidation is carried out by atomic oxygen. The constant for reaction velocity between 15° and 55° varies almost proportionally with the temperature. J. McC.

**Temperature of Maximum Density and Electrical Conductivity of Solutions of Barium Bromide and Iodide, and Calcium Chloride, Bromide, and Iodide.** By LOUIS C. DE COPPET and W. MULLER (*Compt. rend.*, 1902, 134, 1208—1209).—The molecular reduction of the temperature of maximum density is constant or

increases slightly, and, as in the case of the alkali metals, is least for the chlorides and greatest for the iodides. It is greater for barium salts than for the corresponding calcium salts. The molecular conductivity diminishes as the concentration of the solution increases.

C. H. B.

**Lowering of the Freezing Point of Water produced by Concentrated Solutions of Certain Electrolytes, and the Conductivity of such Solutions.** By HARRY C. JONES and FREDERICK H. GETMAN (*Amer. Chem. J.*, 1902, 27, 433—444).—The freezing point and conductivity of solutions of hydrochloric acid, nitric acid, sulphuric acid, potassium hydroxide, calcium chloride, strontium chloride, barium chloride, sodium nitrate, and potassium nitrate up to 3*N* have been determined. Except in the cases of the last two compounds, a minimum has been found for the molecular lowering of the freezing point. The molecular conductivities increase quite regularly, showing no trace of a minimum point. The theoretical discussion is reserved for a later paper.

J. McC.

**The Temperature Coefficients of the Ions in Water. A Law applicable to the Univalent Elements.** By FRIEDRICH KOHLRAUSCH (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 572—580).—It has already been shown (*ibid.*, 1901, 1026) that the temperature coefficient of univalent positive ions is a function of their mobility. As it appeared strange that this should apply only to positive ions, a re-investigation has been made of the negative ions and of some of the doubtful positive ions. The results indicate that the law is quite generally applicable to univalent ions and consequently the ratio of the ionic mobilities approaches the value 1 as the temperature rises.

The temperature coefficient of univalent and bivalent ions is discussed and its bearing on the Hittorf transport numbers; the influence of temperature on the transport ratio can be more accurately ascertained from these coefficients than by direct measurement.

The similar relationship for all univalent ions between mobility and temperature coefficient leads the author to a discussion of the connection between dissolved substance and solvent. The influence of temperature being the same in all cases suggests that the ion is surrounded by an envelope of water which moves with it, and this view is supported by a consideration of the electrical resistance and internal friction of solutions. This hypothesis, however, does not explain why the ions when arranged according to their mobilities fall into the series: Li, Na, Ag, K, Tl, Rb, Cs.

J. McC.

**Methods of Determining the Heat of Solution at the Point of Saturation.** By ED. VON STACKELBERG (*Zeit. physikal. Chem.*, 1902, 42, 96—100).—In reference to a paper by Holsboer (this vol., ii, 226), who prefers van Deventer's method to the author's, the latter argues in favour of his own method, and concludes that the objections to it urged by Holsboer are not valid.

J. C. P.

**Polymerisation and Heat of Formation of Zinc Oxide.** By ROBERT DE FORCRAND (*Compt. rend.*, 1902, 134, 1426—1429).—Previous determinations of the heat of formation of zinc oxide have given

values varying between 83.28 Cal. and 88.2 Cal. ( $\text{Zn} = 65$ ). The author has redetermined this value by measuring the heat of dissolution of zinc in dilute sulphuric acid, and that of zinc oxide in the same acid. For zinc oxide, prepared by dehydrating the crystalline zinc hydroxide at  $125^\circ$  in a current of dry air, the heat of solution is 27.92 Cal.; for the oxide obtained by heating the nitrate at  $350^\circ$  for 4 hours, the heat of solution is 25.23 Cal.; for the oxide prepared from the precipitated hydroxide, the heat of solution is 23.91 Cal. In this case, it was necessary to heat the hydroxide at a very high temperature in order to remove the last traces of water. When zinc oxide is produced by burning zinc in oxygen, the heat of solution is 23 Cal. A determination of the heat of solution of zinc in sulphuric acid gave the value 39.31 Cal.

Hence the heat of formation of zinc oxide from solid zinc and gaseous oxygen varies from 80.29—84.7 Cal., according to the temperature which has been attained in the preparation of the oxide; the higher the temperature the greater the heat of formation.

The view is expressed that the oxide undergoes polymerisation when it is heated, and that the difference between the extreme values of the heat of formation, 4.41 Cal., expresses the heat developed in this process. A specimen of the oxide which has been heated to bright redness, whether cooled rapidly or slowly or kept for a long time, still remains in a polymerised state.

K. J. P. O.

**Ammoniacal Cupric Oxide.** By ALBERT BOUZAT (*Compt. rend.*, 1902, 134, 1310—1312).—The heat of neutralisation was determined of a solution containing 1 gram-mol. of cupric oxide and 28 mols. of ammonia in 14 litres. With 1 mol. of sulphuric acid, the heat evolved is 35.5 Cal.; with 2 mols. of hydrochloric acid, 32.1 Cal.; with 2 mols. of nitric acid, 31.8 Cal.; and with 2 mols. of acetic acid, 30.0 Cal. In each case, the heat of neutralisation is greater than the heat of neutralisation of the cupric oxide or of the ammonia alone, which proves that the acid molecule neutralises a complex base.

The heat of formation of  $\text{CuO}, 28\text{NH}_3$  (dissolved) from solid cupric oxide and ammonia solution is calculated to be about 4.2 Cal. The complex ammoniacal cupric oxide is a strong base.

J. McC.

**Melting of Binary Solid Mixtures by Cooling.** By HENDRIK W. BAKHUIS ROOZEBOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 4, 636—639).—A case is cited of a binary liquid mixture which first solidifies on cooling, then partially liquefies by further fall of temperature.

Azoxyanisole at  $114^\circ$  passes into the condition of liquid crystals, and at  $135^\circ$  changes to an isotropic, clear, yellow liquid; quinol melts at  $169^\circ$ . In the liquid condition, these substances are completely miscible at temperatures lying above the line joining their melting points on a system of coordinates, where the composition is represented along the abscissæ and the ordinates are temperatures. Below this line, the mixing limits are represented by three straight lines, *CH*, *HK*, and *KD*. *C* is the melting point of azoxyanisole, *H* represents the temperature,  $111.6^\circ$ , and a mixture containing 11 mols. per

cent. of azoxyanisole,  $K$  represents  $106^{\circ}$  and a mixture of 25 mols. per cent. of azoxyanisole, and  $D$  is the melting point of quinol. The transition point of solid into liquid crystals of azoxyanisole is depressed by the addition of quinol. Starting with a mixture containing about 10 mols. per cent. of azoxyanisole at  $111.6^{\circ}$ , the formation of liquid mixed crystals first takes place; on further cooling, the mixture solidifies and then again liquefies. The second liquid formed has, however, a different composition.

If the liquid crystalline condition be considered as solid (and the author believes that there are sound reasons for this view), the above phenomenon is one of retrograde solidification.

Another case has been found by Heycock and Neville with mixtures of copper and tin. J. McC.

**Vacuum Distillation.** By EMIL FISCHER and CARL HARRIES (*Ber.*, 1902, 35, 2158—2162).—A mercury air pump is too slow in its action to enable distillations to be carried out satisfactorily under smaller pressures than 0.5 mm.; this disadvantage is especially marked in cases where easily volatile substances such as ether, alcohol, and hydrocarbons are present. By using a "Geryk" vacuum pump (Fleuss' patent), however, and a second receiver cooled by liquid air, wherein all ordinary vapours and gases are condensed, distillations can be readily carried out under pressures not exceeding 0.1—0.2 mm. The receiver in which the distilled substance condenses is cooled with ice and is connected directly to the distilling flask, and to the second receiver which is kept surrounded by a Dewar's vacuum vessel filled with liquid air. The pressure is measured by a MacLeod—Kahlbaum manometer. The original should be consulted for details as to the arrangement of the parts and the stopcocks; the latter are of such a nature as to allow of the receiver being changed without interrupting the vacuum.

In order to ascertain the effectiveness of the apparatus, distillations were carried out with oleic acid, stearic acid, glycerol and  $\alpha$ -methyl-glucoside; that the formation of gaseous decomposition products during distillation does not lower the vacuum is well shown by the results obtained on distilling dry Para rubber. On removing the vessel of liquid air, however, the pressure immediately rose from 0.2 to 15—20 mm. W. A. D.

**Liquefaction of Gaseous Mixtures.** By J. P. KUENEN (*Zeit. physikal. Chem.*, 1902, 41, 43—51).—A criticism in the first place of Caubet's recent paper (this vol., ii, 382), and indirectly of Duhem's theoretical work. J. C. P.

**Solubility of Analogous Salts.** By W. O. RABE (*Zeit. anorg. Chem.*, 1902, 31, 154—157).—Rossi has shown that the ratio between the molecular weights of two salts of the same acid containing two chemically similar metals of the same periodic group is a simple multiple of the ratio of their solubilities. The author has investigated

the solubilities of thallous nitrate, sulphate, chlorate, perchlorate, and picrate and compared them with the corresponding values for lithium, sodium, silver, and ammonium salts without finding any regularity. Comparison with potassium salts, however, shows a most striking similarity, for the molecular solubilities exhibit a very simple relationship.

As the temperature rises, the saturated solutions of thallous and potassium salts become more nearly equimolecular. As the molecular magnitude of the anion increases, there is also a tendency for the saturated solutions to become more nearly equimolecular. J. McC.

**Theory of the Velocity of Chemical Reactions.** By RUDOLF WEGSCHEIDER (*Zeit. physikal. Chem.*, 1902, 42, 62—70).—A reply to Euler (this vol., ii, 384). J. C. P.

**Relative Velocities of the Ions in Solutions of Silver Nitrate in Pyridine and Acetonitrile.** By HERMAN SCHLUNDT (*J. Physical Chem.*, 1902, 6, 159—171).—Solutions of silver nitrate in pyridine and acetonitrile were prepared, and the ion velocities determined by the analyses of the electrode liquids. The following table gives the results obtained, the values in other liquids being added for completeness; the numbers given are the transference numbers of the cation multiplied by 100 :

Solvent.	Volume in litres per gram-mol. of AgNO <sub>3</sub> .							
	0.42.	1.	2.	4.	10.	16.	35.	40.
Water .....	53.2	50.0	48.3	47.3	—	—	—	47.5
Acetonitrile .....	—	38.3	—	42.2	44.8	—	47.3	—
Pyridine .....	—	32.6	34.2	—	39.0	—	—	44.0
Methyl alcohol .....	—	—	—	—	—	53.3	—	—
Ethyl alcohol.....	—	—	—	—	40.5	49.0	—	—

It is seen that the values differ considerably but appear to converge with increasing dilution; data are not available to determine whether this is general in solutions. In aqueous solutions, the values decrease on dilution, in pyridine they increase. This increase is frequently observed in aqueous solutions in the case of compounds which form hydrates, and in this connection it is noteworthy that silver nitrate forms definite compounds with pyridine. L. M. J.

**Velocity of Formation of Simple Ethers.** By M. ROSENFELD FREIBERG (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 422—430).—In continuation of the work of Zagrebin (*ibid.*, 1898, 30, 711), the author has determined the velocities with which various alcohols act on the

esters of benzenesulphonic acid to produce simple ethers together with benzenesulphonic acid. The following table gives the velocities of reaction for the different cases :

Benzenesulphonic esters.	Alcohols.					
	Methyl.	Ethyl.	Propyl.	<i>iso</i> Butyl.	<i>iso</i> Amyl.	Octyl.
Methyl .....	3019	1562	1137	772	827	—
Ethyl .....	2311	1130	816	498	546	420
<i>iso</i> Butyl .....	584	228	171	96	115	—
<i>iso</i> Amyl .....	608	268	195	123	137	—

The relations of these numbers to the structure of the benzenesulphonic esters and to the alcohols are discussed. T. H. P.

**Saponification of the Esters of Carboxylic and Sulphonic Acids.** By RUDOLF WEGSCHEIDER (*Zeit. physikal. Chem.*, 1902, 41, 52—61).—In the author's view, the saponification of the sulphonic esters by water is not accelerated by hydrogen ions,—a contrast to the case of the carboxylic esters; acids have an accelerating influence only when they induce a secondary reaction which takes place with moderate rapidity (compare Kastle, Murrill, and Frazer, *Abstr.*, 1898, i, 140). Alkalis exert an accelerating influence on the rate of saponification, and the hydroxyl ions may be supposed either (1) to act independently of the water, or (2) to have a catalytic influence on the water.

If saponification by water is attributed in all cases to the hydroxyl ions, it is necessary to attribute an accelerating catalytic influence to the hydrogen ions; this influence in the case of the sulphonic esters is proportional to the concentration of the hydrogen ions, in the case of the carboxylic esters to the square of their concentration. The author formulates his views in a series of equations, and he finds experimental verification of them in the work of Kastle, Murrill, and Frazer (*loc. cit.*). J. C. P.

**Influence of Side Chains on the Properties of Carbon Compounds with Open or Closed Chains. VII. Velocity of Combination of Heterocyclic Compounds with Alkyl Bromides.** By NICOLAI A. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 411—422).—The table on p. 494 gives the velocities of combination of allyl and methyl bromides with various derivatives of pyridine, piperidine, quinoline, and *iso*quinoline.

The author proceeds to discuss these results in comparison with those obtained with benzene compounds. Taken together with the numbers given in the author's earlier communications, those here given show that the influence of the side chain on the velocity of combination



	With C <sub>3</sub> H <sub>5</sub> Br.	With CH <sub>3</sub> Br.		With C <sub>3</sub> H <sub>5</sub> Br.	With CH <sub>3</sub> Br.
Pyridine .....	276	578	Quinoline .....	29	96
$\alpha$ -Picoline .....	55	213	<i>iso</i> Quinoline .....	365	645
$\beta$ -Picoline .....	435	—	Quinaldine .....	—	23
Aldehydecollidine	65	346	Lepidine .....	—	159
Piperidine .....	20575	35692	<i>o</i> -Toluquinoline .....	0	0
$\alpha$ -Pipcoline .....	6826	—	<i>m</i> -Toluquinoline .....	0	76
$\delta$ -Coniine .....	2684	10485	<i>p</i> -Toluquinoline ..	34	115
$\beta$ -Pipcoline .....	28109	—	Xyloquinoline .....	0	—
			Hydroquinoline .....	300	177
			Hydro- <i>o</i> -toluquinoline ...	284	187
			Hydro- <i>m</i> -toluquinoline...	349	247
			Hydro- <i>p</i> -toluquinoline ...	610	368

of all compounds—both with open and closed chains and those containing only carbon as well as the hetero-atomic ones—with alkyl haloids exhibits uniform and analogous relations.

T. H. P.

**Influence of Constitution on the Affinity Constants of Organic Acids.** By RUDOLF WEGSCHEIDER (*Monatsh.*, 1902, 23, 287—316. Compare Abstr., 1895, ii, 310).—The author has tabulated the factors which represent the influence of various substituting groups, on the affinity constants of saturated fatty and of aromatic acids. The factors for halogens decrease generally from chlorine to iodine. For a negative substituting group in the fatty series, the factor diminishes rapidly with change of the group from the  $\alpha$ - to the  $\beta$ -position, and then slowly to the  $\delta$ -position, after which it remains almost constant. This seems to throw doubt on the usually accepted views as to the stereoproximity of the  $\gamma$ - and  $\delta$ -positions to the carboxylic group. The influence of a methyl or ethyl group in the  $\alpha$ -position is greatest when replacing a hydrogen atom of a methylene group, least when of a methenyl group; in the  $\beta$ -position an alkyl radicle has a negative influence which gradually changes to positive as the radicle is removed further from the carboxylic group; the influence of a methyl group in the benzene series varies in similar manner, becoming positive in the *meta*- and *para*-positions; hydroxyl and methoxyl show similar changes in the nature of their influence. The influence of the *ortho*-position resembles that of the  $\beta$ , of the *meta* and *para*, that of the  $\gamma$ .

The factor representing the influence of the carboxylic group is found by dividing the affinity constant of one of the carboxylic groups of a dibasic acid by the affinity constant of acetic acid; the product represents the influence of the other carboxyl as a substituting group.

Considerable differences between the calculated and the determined affinity constants are found in the case of acids of the malonic type, having a strongly negative group or no hydrogen attached to the  $\alpha$ -carbon atom, of derivatives of succinic acid in which an alkyl group has replaced a hydrogen atom of each methylene, and of aromatic acids

with substituting groups in the position 2:6 or 2:3 ( $\text{CO}_2\text{H}=1$ ), in the latter case when  $\text{NO}_2$  or  $\text{CO}_2\text{Et}=2$ . Substitution in both *ortho*-positions sometimes weakens the negative influence of the single substituting group.

G. Y.

**Catalysis of Hydrazine.** By SIMEON TANATAR (*Zeit. physikal. Chem.*, 1902, 41, 37—42).—In a previous paper (this vol., ii, 386), it was shown that the catalysis of hydrazine sulphate by platinum in aqueous solution takes place according to the equation  $3\text{N}_2\text{H}_4 = 4\text{NH}_3 + \text{N}_2$ . In the present paper, it is shown that free hydrazine in aqueous solution and in the presence of platinum breaks up in the following manner:  $2\text{N}_2\text{H}_4 = 2\text{NH}_3 + \text{N}_2 + \text{H}_2$ , the evolved gas consisting of equal volumes of nitrogen and hydrogen. In the presence of sodium hydroxide the decomposition of free hydrazine is different, namely,  $3\text{N}_2\text{H}_4 = 2\text{NH}_3 + 2\text{N}_2 + 3\text{H}_2$ , the evolved gas containing 60 per cent. of hydrogen. If, however, sodium hydroxide is added to hydrazine sulphate in equivalent quantity, the evolved gas contains only 9—10 per cent. of hydrogen; if the quantity of sodium hydroxide is increased, the proportion of hydrogen rises, but only in the presence of a large excess of alkali does it amount to 60 per cent.

J. C. P.

**Synthetic Analysis of Solid Phases.** By WILDER D. BANCROFT (*J. Physical Chem.*, 1902, 6, 178—184).—The determination of the composition of an alloy, which separates from mother liquor, is frequently difficult, owing to the presence of the mother liquor mixed with the crystals. The author suggests the addition of a third substance which will not enter into the alloy. Then, if the original composition is  $x_1$  grams of *A*, and  $y_1$  grams of *B* per gram of *C*, and that of the liquor is  $x_2$  grams of *A*, and  $y_2$  grams of *B* per gram of *C*, then the composition of the alloy is  $x_1 - x_2$  grams of *A* to  $y_1 - y_2$  grams of *B*. Even if the third substance forms part of the solid phase, the method is still available, as if, in a triangular diagram, points representing the initial and final concentrations of the liquor be taken, the composition of the alloy is represented by a point in the extension of the line joining the two points, and a second experiment with a different initial concentration serves to determine the alloy. The author indicates how by these means the equilibrium field of a three-component system may be investigated.

L. M. J.

**Equilibria in Systems of Three Components, the Formation of Two Liquid Phases being possible.** By P. A. MEERBURG (*Zeit. physikal. Chem.*, 1902, 40, 641—688).—An investigation on the lines of Schreinemakers' work. The systems chosen were (1) triethylamine-water-ethyl alcohol; (2) triethylamine-water-ether; (3) triethylamine-water-phenol. According to Schreinemakers, the binodal curves for higher temperatures may (1) be enclosed by those for lower temperatures—as for the system water-phenol-acetone (Schreinemakers, *Abstr.*, 1900, ii, 393); or (2) enclose those for lower temperatures; an example of this latter case has been found by the author in the system amine-water-alcohol. In the other two systems investigated—amine-water-ether and amine-water-phenol—the binodal curves for different tem-

peratures cut one another and the field of heterogeneous equilibrium is displaced, as in the case of water, alcohol, and sodium sulphate, studied by de Bruyn (*Abstr.*, 1900, ii, 266).

Full details are given of the composition of the phases in equilibrium with one another at different temperatures, and the results are expressed by the usual graphical methods.

J. C. P.

**Limitations of the Mass Law.** By WILDER D. BANCROFT (*J. Physical Chem.*, 1902, 6, 190—192).—The dissociation of a compound in solution has been deduced from that of the vapour in cases where Henry's law holds. Thus, if the solubility relations of  $AB$ ,  $A$  and  $B$  are  $c_1 = k_1 c'_1$ ,  $c_2 = k_2 c'_2$ ,  $c_3 = k_3 c'_3$ , and the equilibrium equation is  $Kc_1 = c_2 c_3$ , then for equilibrium in solution  $(K.k_1/k_2 k_3) c'_1 = c'_2 c'_3$ . The author shows, however, that this will not hold if, as is frequently the case, the solubility of  $A$  is affected by the presence of  $AB$  or  $B$ .

L. M. J.

**The so-called Negative Nature of Unsaturated Radicles.** By DANIEL VORLÄNDER (*Ber.*, 1902, 35, 2309—2313).—A reply to Henrich (this vol., ii, 449).

W. A. D.

**Relation between Crystalline Form and Molecular Structure.** By H. ZIENGIEBL (*Zeit. Kryst. Min.*, 1902, 36, 117—150).—Various substances which show great similarity in crystalline form without being isomorphous are compared. Thus, in the replacement of the groups  $CO$  and  $SO_2$  in orthosulphobenzoic and phthalic acids, in benzenesulphonic and benzoic acids, &c., and in various salts of these; the replacement of  $CH_2$  and  $NH$  in methanedisulphonic acid and imino-sulphonic acid; of oxygen and halogens in salts of iodic and fluoro-iodic acids, &c. Detailed crystallographic determinations were made on many of these substances to enable the comparisons of the crystallographic axes, topic axes, &c., to be made.

L. J. S.

**A Method for Separating Crystals from Alloys.** By CORNELIS VAN EYK (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 4, 758—761).—Objection is taken to the methods which have previously been used for this purpose.

The temperature at which crystals begin to separate from the molten alloy is first determined, then about 30 grams of the alloy are placed in a hard-glass test-tube which has a capillary constriction in the centre; if necessary, a small plug of asbestos can be inserted above this. The tube is evacuated, then sealed and placed in a specially constructed electric furnace capable of heating it to the required temperature. The furnace is set in a properly adapted centrifugal machine, and after rotating it is found that the liquid part of the alloy has passed into the lower portion of the tube, whilst the crystals are retained in the upper part.

Experiments are described to prove the efficiency of the method. For temperatures up to  $300^\circ$ , no greater difference than  $2^\circ$  has been observed before and after rotation. The crystals cannot be completely freed from mother liquor, but the method easily indicates whether pure metals, compounds, or mixed crystals are deposited from the alloy.

J. McC.

**Plasticity of Clay.** By PAUL ROHLAND (*Zeit. anorg. Chem.*, 1902, 31, 158—160).—The cause of the plasticity of clay has not yet been satisfactorily explained. The author questions the mechanical explanations which have been offered; he suggests that those substances which exhibit plastic properties all contain colloids, and that the plasticity is connected with the peculiar action of water on colloidal substances.

J. McC.

**Calculation of Atomic Weights.** By JOSEF SCHMIDT (*Zeit. anorg. Chem.*, 1902, 31, 146—153).—If it be assumed that chemical attraction obeys the same laws as the attraction of bodies, a numerical series of atomic weights can be obtained. The author assumes that every chemical valency corresponds with a determinate part of the atomic weight and that the atom consists of an active part and of an inactive part. The inactive part is represented by  $a$  and each active part by  $b$ , so that the atom of an univalent element is  $a + b$  and that of a bivalent element  $a + 2b$ . For the series from lithium to fluorine, the fundamental numbers are:  $a = 2$ ,  $b = 5$ ; for the series from sodium to chlorine,  $a = 14$ ,  $b = 7$ ; for the series from potassium to manganese,  $a = 23$ ,  $b = 12$ ; for the series from copper to bromine,  $a = 36$ ,  $b = 18$ . Attention is called to certain regularities with respect to these fundamental numbers. In some cases (heavy univalent elements), it is necessary to assume that the atom is weighted too much on one side by the chemical attraction and to balance this the atom contains a loosely bound excess weight which for sodium amounts to 2.

J. McC.

**The Periodic System and the Properties of Inorganic Compounds. IV. The Solubility of Double Sulphates of the Formula  $M'M''(SO_4)_2 \cdot 6H_2O$ .** By JAMES LOCKE (*Amer. Chem. J.*, 1902, 27, 455—481).—The salts examined contain alkali metals, except sodium and lithium, ammonium, or thallium, as  $M'$ , whilst  $M''$  was magnesium, zinc, cadmium, iron, nickel, cobalt, manganese, or copper. The solubilities do not follow the same order as the atomic weights. The influence of each metal on the solubility is specific and independent of the atomic weight; it is retained throughout all the compounds.

The relation between the solubilities of corresponding salts of any two bivalent metals can be accurately expressed by the equation  $y' = ay + 2by + c$ , where  $y$  and  $y'$  are the salts of two bivalent metals with the same univalent metal. The values for the coefficients  $a$ ,  $b$ ,  $c$  are calculated for a number of pairs of bivalent metals and with the aid of these the solubilities of other salts can be predicted. The applicability of an equation of this type proves that in a group of isomorphous compounds the effect of a given element on the solubility of its compounds in the series is constant throughout these compounds.

As these solubility relationships do not agree with the positions of the elements in the periodic arrangement, the author is of the opinion that for the systematisation of inorganic compounds a new classification is required which will properly represent the quantitative relationships and include radicles as well as elements.

J. McC.

Lecture Experiments illustrating Various Types of Catalytic Action. By ALBERT A. NOYES and G. V. SAMMET (*J. Amer. Chem. Soc.*, 1902, **24**, 498—515).—Experiments are described to demonstrate the various types of catalytic action, namely, catalysis by carriers, by adsorbent contact agents, by electrolytic contact agents, by water, by dissolved electrolytes, by enzymes, and by inorganic colloids. For details, the original must be consulted. E. G.

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## Inorganic Chemistry.

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**Halogen Salts.** By PAUL PFEIFFER (*Zeit. anorg. Chem.*, 1902, 31, 191—234).—Werner (Abstr., 1899, ii., 278) has instituted a comparison of the chloro-salts and has shown that these can be classed in one system in accordance with the theory formulated by him. In order to complete the examination, the author has collected details of all the complex bromides and iodides which have been described, and shows that these are quite analogous to the corresponding chlorides. They can be grouped in Werner's system, and it is pointed out that the existence of certain of them completely disproves Remsen's theory of double salts. A list is given of 202 bromides and 175 iodides.  
J. McC.

**Behaviour of Hydrogen Chlorides and Fluoride towards Caro's Reagent.** By EDGAR WEDEKIND (*Ber.*, 1902, 35, 2267—2269).—Caro's reagent liberates chlorine from aqueous or gaseous hydrogen chloride, and bromine from hydrogen bromide. Attempts to prepare fluorine by oxidising hydrogen fluoride with Caro's reagent under a variety of conditions gave only negative results.  
T. M. L.

**Atomic Weight of Iodine.** By ALBERT LADENBURG (*Ber.*, 1902, 35, 2275—2285).—Iodine, when purified by Stas' method, is liable to contain traces of chlorine. Three experiments on the conversion of silver iodide into chloride gave for the atomic weight of iodine the values 126·957, 126·961, 126·963, mean 126·960, with an error of  $\pm 0\cdot0003$  ( $\text{Ag}=107\cdot93$ ,  $\text{Cl}=35\cdot45$ ), Stas' value being 126·85. A determination by converting silver into nitrate and then into iodide gave, after correcting for the chlorine in the potassium iodide, the value 126·87, but this is considered less accurate.  
T. M. L.

**Physical Properties of Hydrogen Telluride.** By ROBERT DE FORCRAND and HENRI FONZES-DIACON (*Compt. rend.* 1902, 134, 1209—1211).—Hydrogen telluride is readily obtained by the action of water, or better, of acids, and especially of metaphosphoric acid, on aluminium telluride,  $\text{Al}_2\text{Te}_3$ , which is prepared by igniting an intimate mixture of aluminium and tellurium by means of magnesium. Deter-

minations of the physical constants of the gas were made with the following results: boiling point,  $0^{\circ}$ ; melting point,  $-48^{\circ}$ ; density of the liquid, 2.57; molecular volume, 49.75. These values do not form a regular series with the corresponding values for oxygen, sulphur, and selenium.

C. H. B.

**The Densities of Mixtures of Hydrazine and Water.** By J. W. DITO (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 4, 756—758).—The sp. gr. of a series of mixtures of hydrazine and water has been determined. Pure hydrazine has the sp. gr. 1.0114 at  $15^{\circ}/4^{\circ}$ , and as water is added the sp. gr. increases up to 1.0470, obtained when the mixture contains 64.1 per cent. of hydrazine; it then falls continuously. The composition of the liquid with maximum sp. gr. corresponds almost exactly with  $N_2H_4 \cdot H_2O$ .

J. McC.

**Preparation of Gaseous Hydrogen Phosphide.** By F. BODROUX (*Bull. Soc. Chim.* 1902, [iii], 27, 568—569).—The method is essentially the same as that of Matignon (*Abstr.*, 1900, ii, 482), but the initial product is less pure and is more easily obtained. A mixture of two parts of aluminium powder and one part of red phosphorus is made and the mass inflamed; among other things, aluminium phosphide is formed. The mass is then treated with cold or lukewarm water (not above  $50^{\circ}$ ), whereby the aluminium phosphide is slowly decomposed with evolution of pure hydrogen phosphide. In this experiment, the aluminium may profitably be replaced by magnesium.

A. F.

**Atomic Weight of Arsenic.** By W. CLARENCE EBAUGH (*J. Amer. Chem. Soc.*, 1902, 24, 489—497).—Silver arsenate was converted into silver chloride by heating it in a stream of hydrogen chloride; the mean of eight determinations gave 75.004 as the atomic weight of arsenic, the probable error being  $\pm 0.012$ . The silver chloride thus obtained was reduced to silver by heating it in a current of hydrogen; from seven determinations a mean value of 74.975 was obtained, with a probable error of  $\pm 0.015$ . The results obtained by the conversion of silver arsenate into silver bromide were not mutually concordant. Eight estimations of the lead chloride produced by heating the arsenate in hydrogen chloride gave a mean value 75.022, with a probable error of  $\pm 0.009$ . The value obtained as the mean of three estimations of the lead bromide formed from lead arsenate was 75.004, with a probable error  $\pm 0.021$ . The mean value for the atomic weight of arsenic from the whole of the experiments was 75.008, and the probable error  $\pm 0.006$ . ( $O = 16.0$ )

E. G.

**Action of Hydrogen Peroxide on Sodium Arsenate ( $Na_3AsO_4$ ).** By G. I. PETRENKO (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 391—392).—The interaction of hydrogen peroxide and sodium arsenate yields a compound of the composition  $Na_3As_3O_{17} \cdot 21H_2O$ , which may be regarded as a hydrate of sodium arsenate in which part of the water is replaced by hydrogen peroxide:  $3Na_3AsO_4 \cdot 5H_2O_2 \cdot 16H_2O$ .

T. H. P.

**Method of Collecting Solid Carbon Dioxide for Lecture Purposes.** By CHARLES R. DARLING (*Chem. News*, 1902, 85, 301—302).—A flannel bag, made by rolling coarse flannel round a stout tube or rod and tying up one end, is tied by the other end on to the nozzle of a cylinder of carbon dioxide. When the gas is turned on, a rod of solid carbon dioxide soon forms, and can be easily removed by undoing the bag or cutting it open. D. A. L.

**Action of Hydrogen Peroxide on Carbonates.** By P. KAZAN-EZKY (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 388—391. Compare this vol., ii, 317).—The action of hydrogen peroxide on potassium carbonate yields two compounds having compositions represented by the formulæ  $K_2CO_3 \cdot 2H_2O_2 \cdot \frac{1}{2}H_2O$  and  $K_2CO_3 \cdot 3H_2O_2$ ; the author ascribes to them the constitutions  $(K \cdot O \cdot O \cdot O)_2CO \cdot 2\frac{1}{2}H_2O$ , and  $(K \cdot O \cdot O \cdot O)_2CO \cdot 3H_2O$  respectively. T. H. P.

**Colloidal Silver.** By CARL PAAL (*Ber.*, 1902, 35, 2224—2236).—Colloidal silver is formed whenever a solution of colloidal silver oxide is reduced, for example, by hydrazine hydrate. It is best prepared by adding silver nitrate to an alkaline solution of sodium protalbate or lysalbate (this vol., i, 653), warming the mixture at 100° until the reduction is complete, and then evaporating after removal of the inorganic salts by dialysis. By using large quantities of silver nitrate and sodium lysalbate, a solid product was obtained on acidifying with acetic acid, containing 90 per cent. of colloidal silver. This mixture was soluble in alkalis, but loses this solubility in part on keeping. The solutions of colloidal silver have a characteristic colour, and the solid is grey or black, with a steel blue or greenish-blue lustre. This form of colloidal silver is far more stable than the commercial form (collargol), a solution of which can neither be evaporated nor frozen, without reconversion of silver into the ordinary form. K. J. P. O.

**Colloidal Silver Oxide.** By CARL PAAL (*Ber.*, 1902, 35, 2206—2218).—When aqueous potassium or sodium hydroxide is added to a suspension of silver protalbate or lysalbate (this vol., i, 653), the whole of the solid dissolves. The silver appears to be present as colloidal silver oxide, as not only does the solution show none of the ordinary reactions of silver, but on dialysis the alkali salt of protalbic or lysalbic acid diffuses, but no silver, until ammonia has been added, when the soluble ammoniacal compound of silver oxide diffuses. A very concentrated solution of this colloidal oxide can be prepared by adding silver nitrate to the solution obtained as above, until a precipitate is formed, and then sufficient aqueous potassium hydroxide to again dissolve it. After removing the alkali nitrate by dialysis, a mixture of alkali protalbate and colloidal silver oxide may be obtained by pouring the solution into alcohol or evaporating it at a low temperature. This mixture is pure white when obtained by precipitation, but nearly black when prepared by evaporation. Both specimens retain the faculty of being soluble in water for a very long period. When first prepared, the solutions are colourless, but soon become dark, probably from the conversion of the colloidal silver



hydroxide first formed into the colloidal oxide. Hydrazine hydrate reduces the oxide to colloidal silver.  
K. J. P. O.

**Combining Weight of Calcium. II.** By F. WILLY HINRICHSSEN (*Zeit. physikal. Chem.*, 1902, 40, 746—749. Compare this vol., ii, 137).—The combining weight of calcium has been determined by the ignition of calcspar from a Russian source, this calcspar containing 0.012 per cent. of silica and 0.054 per cent. of iron. The values obtained for the atomic weight of calcium were 40.139 and 40.136. In the author's method of ignition, care is taken to prevent any loss of the oxide by sublimation, and probably neglect of this precaution is responsible for the low values obtained by previous workers.  
J. C. P.

**Hydrated Barium Silicate.** By W. WAHL (*Zeit. Kryst. Min.*, 1902, 36, 156—160).—Optical and goniometric measurements were made on crystals formed in a glass bottle in which barium hydroxide had been left for about a dozen years. The crystals are rhombic and reach a length of 7 mm.; sp. gr. 2.585 and 2.604; their composition is  $\text{BaSiO}_3 \cdot 6\text{H}_2\text{O}$ . Water is lost in dry air, and all except 1 molecule is expelled below  $180^\circ$ ; the formula may therefore be written as  $\text{BaH}_2\text{SiO}_4 \cdot 5\text{H}_2\text{O}$ . Small crystals of the same substance, which is analogous to the zeolites, were obtained by the action of barium hydroxide on amorphous silica.  
L. J. S.

**Preparation of Arsenic-free Zinc.** By OTTO HEHNER (*J. Soc. Chem. Ind.*, 1902, 21, 675—676).—A few pounds of ordinary zinc are melted in a clay crucible over a gas fire and a piece of sodium is added, using for each pound of zinc about 1 gram of sodium at a time. The molten metal is stirred with a piece of hard glass tubing bent at right angles; an iron rod should not be used on any account. After removing the scum with a porcelain spoon, another piece of sodium is introduced and the mass stirred and skimmed as before. Finally, the metal is poured into a second crucible and the treatment with sodium repeated once more. When the mass has considerably cooled, the metal is granulated by pouring into water, best containing a very little acid.  
L. DE K.

**Action of Solid Substances on one another.** By J. MATUSCHEK (*Chem. Zeit.*, 1902, 26, 526—527).—Zinc nitrite is formed when dry sodium nitrite and zinc chloride or sulphate, with or without water of crystallisation, are shaken together. The heat developed by the reaction decomposes part of the zinc nitrite to zinc oxide with evolution of brown fumes. With magnesium sulphate or barium chloride, the reaction takes place less easily, but more energetically with the chlorides of aluminium, tin, or iron.  
G. Y.

**Alloys of Cadmium and Magnesium.** By OCTAVE BOUDOUARD (*Compt. rend.*, 1902, 134, 1431—1434. Compare Abstr., 1901, ii, 512).—The melting points of mixtures of cadmium and magnesium, varying in composition from 90 per cent. cadmium to 90 per cent. magnesium, show three maxima ( $500^\circ$ ,  $565^\circ$ , and  $650^\circ$ ) and two

minima ( $400^{\circ}$  and  $560^{\circ}$ ); the three maxima correspond respectively with three compounds,  $\text{CdMg}$ ,  $\text{CdMg}_4$ , and  $\text{CdMg}_{30}$ . The compound  $\text{CdMg}$  was isolated by treating the mixture of 75 parts of cadmium and 25 parts of magnesium with cold aqueous 1 per cent. ammonium chloride, when the alloy is left as a grey, crystalline powder. The compound  $\text{CdMg}_4$  is obtained in a similar manner from the mixture of 53.5 per cent. of cadmium and 46.5 per cent. of magnesium; the third compound was not isolated. By etching the polish surface of mixtures of appropriate composition, crystals of the three compounds just mentioned can be shown to be present. All these alloys are white in colour, are moderately malleable, are permanent in dry air, but are very readily attacked in the presence of water.

K. J. P. O.

**Cuprous Compounds. I.** By GUIDO BODLÄNDER and O. STORBECK (*Zeit. anorg. Chem.*, 1902, 31, 1—41).—An attempt has been made to ascertain the tension required to separate cuprous ions from a normal solution; incidentally, side questions have arisen, such as the degree of dissociation of cuprous salts and the nature of the cuprous ion, ( $\text{Cu}^{\cdot}$  or  $\text{Cu}_2^{\cdot\cdot}$ ). From the solubility of cuprous chloride in water, it is shown that decomposition according to the equation  $2\text{CuCl} \rightleftharpoons \text{CuCl}_2 + \text{Cu}$  (or  $\text{Cu}_2\text{Cl}_2 \rightleftharpoons \text{CuCl}_2 + \text{Cu}$ ) occurs and at the same time hydrolysis takes place. The cuprous copper which is present in the solution does not exist completely as simply cuprous ions, but partly as complex ions formed from chlorine ions and undissociated cuprous chloride as the neutral component. The solubility of cuprous chloride in hydrochloric acid and potassium chloride solutions was also determined. At low concentrations of hydrochloric acid, the quotient  $[\text{Cl}]/[\text{Cu}]$  is nearly constant, therefore at such concentrations the complex ion has probably the composition  $\text{CuCl}_2'$ ; in concentrated solution, the quotient  $[\text{Cl}]^2/[\text{CuCl}_3]$  is constant, and in this case the composition of the complex anion is  $\text{CuCl}_3''$ .

The solubility of cuprous chloride in presence of excess of cupric ions was determined in order to ascertain whether the cuprous ion is  $\text{Cu}^{\cdot}$  or  $\text{Cu}_2^{\cdot\cdot}$ ; on account of the uncertainty of the degree of dissociation of the cupric salt, no definite conclusion could be arrived at.

From the results obtained on the solubility of cuprous chloride on addition of potassium chloride, it is concluded that the compound  $(\text{CuCl})_m\text{KCl}$  is formed. The *E.M.F.* of concentration cells (see Bodländer, *Festschrift für Richard Dedekind*, Brunswick, 1901) containing potassium chloride was determined, and from the results the formation of  $\text{K}_2\text{CuCl}_3$  is confirmed. In solutions of potassium chloride from 0.1 to 0.22*N* the compound  $\text{KCuCl}_2$  is formed and gives the anion  $\text{CuCl}_2'$ .

J. McC.

**Constitution of Cuprammonium Salts; Action of Ammonia.** By ALBERT BOUZAT (*Compt. rend.*, 1902, 134, 1216—1219).—The quantity of heat developed by the action of an excess of ammonia on a dissolved cupric salt of a strong acid is independent of the nature of the acid and is considerably higher than that calculated on the assumption that simple decomposition takes place. It follows that cuprammonium salts are salts of a complex base, and not ordinary basic salts.

C. H. B.

**Copper Chloro-, Bromo-, and Iodo-bismuthites.** By FERNAND DUCATTE (*Compt. rend.*, 1902, 134, 1212—1213).—The action of halogen salts of copper on bismuth sulphide yields bronze-grey, well-crystallised compounds of the type  $2\text{Cu}_2\text{S}, \text{Bi}_2\text{S}_3, 2\text{BiSX}$ , where  $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ . They are stable at the ordinary temperature, but decompose when heated in air, and are attacked by dilute acids with liberation of hydrogen sulphide. The chlorine compound has a sp. gr. 6.78, the bromine compound 6.41, and the iodine compound 6.50.

C. H. B.

**Colloidal Mercuric Oxide.** By CARL PAAL (*Ber.*, 1902, 35, 2219—2223).—When aqueous sodium hydroxide is added to mercuric protalbate or lysalbate, or when mercuric chloride is added to an alkaline solution of the sodium salts of these acids, a solution of colloidal mercuric oxide is obtained, which may be freed from inorganic and some of the organic material by dialysis. The colloidal mercury compound is not dialysable. The solution is yellow in colour and only transparent when in thin layers. On evaporation at a low temperature, a mixture of colloidal mercuric oxide and salts of protalbic or lysalbic acid is formed, which consists of reddish-brown scales and is soluble in water. The solutions of the colloidal oxide are easily reduced, especially under the influence of light, metallic mercury being deposited. With the aid of lysalbic acid, a solid can be obtained containing more than 40 per cent. of colloidal oxide. K. J. P. O.

**Decomposition of Mercury Nitrates by Heating.** By J. MYERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 4, 657—659).—Crystallised mercurous nitrate, when heated, evolves at first a mixture of nitrogen peroxide and nitrogen trioxide, and finally nitric oxide. If the anhydrous salt be used, almost pure nitrogen peroxide is obtained. During the decomposition, a yellow sublimate is formed in the neck of the retort and analysis indicates that this may be a mercurio-mercuric orthonitrate,  $\text{Hg}'_2\text{Hg}''_2(\text{NO}_4)_2$ , derived from orthonitric acid,  $\text{H}_3\text{NO}_4$ . The same substance is produced by heating mercuric nitrate or by heating mercurous nitrate in a vacuum tube. The author supposes that at the high temperature complex molecules  $\text{Hg}_3(\text{NO}_3)_4$  or  $\text{Hg}_4(\text{NO}_3)_8$  suffer decomposition into this mercurio-mercuric orthonitrate with evolution in the former case of  $2\text{NO}_2$ , and in the latter of  $6\text{NO}_2$  and  $2\text{O}_2$ . J. McC.

**Influence of Cerium on Lanthanum containing Didymium and Praseodymium.** By ROBERT MARC (*Ber.*, 1902, 35, 2370—2376).—A sample of ordinary brown didymium oxide, giving none of the ordinary reactions for cerium, was dissolved in hydrochloric acid, the solution being then rendered slightly alkaline and saturated with chlorine. The greater part of the oxide passed into solution, leaving a small, insoluble residue. The soluble and insoluble portions, after being reconverted into oxides, exhibited the same spectral bands and were apparently equally rich in praseodymium. The oxide, obtained from the insoluble residue, had, however, a brown

colour and gave abundant indications of cerium and peroxides; the oxide recovered from the solution, on the other hand, was grey in colour and did not evolve chlorine when treated with hydrochloric acid. On adding 1—2 per cent. of a cerium salt to the solution of the grey oxide and igniting the mixture, a brown product was obtained which resembled the original material in evolving chlorine with hydrochloric acid and giving none of the reactions of cerium.

This separation of didymium from cerium is less easily effected in mixtures of praseodymium, lanthanum and cerium oxides containing only small quantities of neodymium, and it is necessary to repeat the operation four times before a white or pink oxide is obtained which is free from peroxide.

These results indicate that the presence of cerium is necessary for the peroxidation of didymium. Accordingly mixtures containing a definite amount of cerium were prepared by adding varying quantities of cerous salt to the solution of the purified grey didymium oxide, the hydroxides being subsequently precipitated and ignited to oxides. It was found that the amount of peroxide present in the product is rapidly augmented by increasing the percentage of cerium, this element being conveniently estimated by Knorre's method (*Abstr.*, 1900, ii, 576), whilst the peroxide was determined iodometrically after distillation with hydrochloric acid in a current of carbon dioxide. Small quantities of cerium have very little influence on the formation of peroxide, and the action first becomes noteworthy when 2 per cent. of this element is present, the mixture then containing 2.25 per cent. of peroxide. The addition of 5 per cent. of cerium leads to the production of 14.76 per cent. of peroxide; 10 per cent. of this impurity gives rise to 35.89 per cent. of higher oxide, and more than 45.18 per cent. of this product results from the introduction of 15 per cent. of cerium. The specimen of didymium oxide employed contained only about 15 per cent. of praseodymium, so that the final result must be due to the simultaneous peroxidation of the neodymium present. Nevertheless, the addition of cerium to pure neodymium oxide does not induce the formation of peroxide.

A sample of praseodymium prepared by Schottländer gave no spectral bands of neodymium and no indications of cerium; nevertheless, it had a brown colour, and on treatment with hydrochloric acid evolved an amount of chlorine corresponding with 44.12 per cent. of peroxide. It was not found possible to free it from cerium by the above described process, yet the addition of an equal weight of lanthanum oxide entirely prevented the formation of peroxide, whilst half this amount reduced the proportion of higher oxide to 0.50 per cent. Neodymium and lanthanum therefore seem to hinder this peroxidising action of cerium.

Specimens of didymium oxide with 2—10 per cent. of cerium give very faint indications of the latter element when tested with hydrogen peroxide or ammonium persulphate. Since these reactions depend on the conversion of colourless cerous compounds into ceric derivatives, it is extremely probable that the exchange of oxygen between the didymium and cerium oxides occurs even in the hydrated condition and in solutions of their salts.

G. T. M.

**Terbium.** By ROBERT MARC (*Ber.*, 1902, 35, 2382—2390).—An earth obtained in the separation of didymium from monazite by the chromic acid method was freed from neodymium and samarium by precipitating with potassium sulphate, and was then fractionally precipitated with ammonia. During the fractionation, the oxide became darker and finally deep ochre-brown; the erbium absorption spectrum became feebler and finally disappeared, leaving a new band,  $\lambda$  644—641, together with Soret's four holmium-bands,  $\lambda$  454—449, 640, 536, and 522. The atomic weight of the fraction (reckoned on  $R_2O_3$ ) was 158. This could not be altered by fractionation with ammonia, but a further separation was effected by means of the oxalates, the atomic weight ranging from 151.95 to 161.18. The brown colour of the oxide was unaffected by the oxalate fractionation; it is removed by igniting in a stream of hydrogen with loss in weight of 0.069 per cent., whilst a determination by titration of the active oxygen in the same sample gave  $O = 0.075$  per cent.; this would correspond with the presence of about 1.5 per cent. of peroxide-forming earth.

The conclusions drawn are (1) that terbium oxide has an intense ochre-brown colour, (2) that the earths described as terbia have usually been mixtures of yttria with a heavier, colourless, spectrum-free earth, probably ytterbium, and containing only a small amount of terbium oxide, (3) that terbium forms two oxides, of which the higher is coloured (compare praseodymium), and (4) that terbium has a characteristic absorption spectrum, the chief feature of which is the band  $\lambda$  464—461.

T. M. L.

**Preparation of Anhydrous Chlorides of Samarium, Yttrium, and Ytterbium.** By CAMILLE MATIGNON (*Compt. rend.*, 1902, 134, 1308—1310).—Hydrated samarium chloride,  $SmCl_3 \cdot 6H_2O$ , when heated at  $100^\circ$  in a current of dry hydrogen chloride, loses 5 mols. of water, and the sixth mol. after prolonged heating at  $180^\circ$ . The anhydrous salt fuses below  $1000^\circ$  to a brownish liquid. It is easily soluble in water and is very hygroscopic.

Hydrated yttrium chloride,  $YCl_3 \cdot 6H_2O$ , and ytterbium chloride,  $YbCl_3 \cdot 6H_2O$ , both act on polarised light; the former fuses at  $163^\circ$ , the latter at  $150$ — $155^\circ$ . When heated in a current of dry hydrogen chloride, they behave exactly as samarium chloride does, giving in the first place monohydrates, then the anhydrous salts. J. McC.

**Compounds of Anhydrous Aluminium Chloride with Hydrogen Sulphide.** By E. BAUD (*Compt. rend.*, 1902, 134, 1429—1431).—When dry aluminium chloride is heated in a current of dry hydrogen sulphide, a crystalline sublimate is formed which consists of aluminium chloride containing a variable quantity of hydrogen sulphide. At the ordinary temperature, hydrogen sulphide is also absorbed to a certain extent. If the chloride is treated with liquid hydrogen sulphide at  $-70^\circ$  and the liquid allowed to evaporate, a white solid is left which, as the temperature rises from  $-45^\circ$  to the ordinary temperature, gives off 1 mol. of hydrogen sulphide for each mol. of aluminium chloride used. The solid remaining still contains hydrogen sulphide and is a compound,  $Al_2Cl_6 \cdot H_2S$ , which is stable at the ordinary tem-

perature; its dissociation pressure is 760 mm. at about 60°. It is decomposed by water, and its heat of dissolution is +150.56 Cal., therefore the heat of formation of solid  $\text{Al}_2\text{Cl}_6\cdot\text{H}_2\text{S}$  is +9.45 Cal., whereas that calculated by means of Trouton's formula from the dissociation pressure is 9.99 Cal.

K. J. P. O.

**Fluoromolybdates.** By P. KAZANEZKY (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 383—387).—By the action of hydrogen peroxide on the double salt of potassium fluoride with potassium fluoropermolybdate having the composition  $\text{MoO}_3\text{F}_2\cdot 2\text{KF}\cdot\text{H}_2\text{O}$ , the two fluorine atoms of the fluoropermolybdate molecule are first replaced by the peroxide residue,  $-\text{O}-\text{O}-$ , giving a compound of the formula  $\text{MoO}_4\cdot 2\text{KF}\cdot\text{H}_2\text{O}$ . Continued action of the hydrogen peroxide results in the formation of a substance approximating in composition to that of potassium permolybdate.

T. H. P.

**Atomic Weight of Uranium.** By THEODORE W. RICHARDS and BENJAMIN S. MERIGOLD (*Chem. News*, 1902, 85, 177—178, 186—188, 201, 207—209, 222—224, 229—230, 249).—Uranous bromide was prepared by heating urano-uranic oxide in an atmosphere of bromine, the bromide being sublimed, transferred to a weighing bottle, and the bottle stoppered, in a specially devised apparatus which is described, and which permitted all these operations to be performed in an atmosphere of either nitrogen or bromine with the rigorous exclusion of oxygen and hydrogen. The bottle of uranous bromide, after weighing, was opened under water, dilute hydrogen peroxide was added, and the bromine was precipitated in one series by means of excess of silver nitrate, and in another by the addition of the exact weight of silver dissolved in nitric acid. From the first series, the mean number 238.54, from the second series, 238.52, was obtained for the atomic weight of uranium, the molecular weight of silver bromide being taken as 187.885. A correction is made for the amount of sodium bromide in the uranous bromide. The extreme numbers in the authors' final six analyses are  $\text{U} = 238.46$  and  $238.60$ , the mean being 238.53 ( $\text{O} = 16$ ;  $\text{Br} = 79.955$ ).

D. A. L.

**Octa-hydrated Uranium Sulphate.** By N. A. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 381—383).—This salt,  $\text{U}(\text{SO}_4)_3\cdot 6\text{H}_2\text{O}$ , can be obtained in well-developed crystals by the action of sunlight on a solution of  $\text{UO}_2\text{SO}_4$  in alcohol.

T. H. P.

**Characteristics of Compounds of Quadrivalent Uranium.** By N. A. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 375—380).—The author has obtained well-crystallised uranium compounds of the following compositions:  $\text{U}(\text{C}_2\text{O}_4)_2\cdot 6\text{H}_2\text{O}$ ;  $2\text{U}(\text{C}_2\text{O}_4)_2\cdot \text{K}_2\text{C}_2\text{O}_4\cdot 8\frac{1}{2}\text{H}_2\text{O}$ ; and  $\text{UCl}_4\cdot \text{UO}_2\cdot 2\text{NaCl}\cdot 6\text{H}_2\text{O}$ .

T. H. P.

**Ammonium Vanadicophosphotungstate.** By EDGAR F. SMITH and FRANZ F. EXNER (*J. Amer. Chem. Soc.*, 1902, 24, 573—578).—During the investigation of a large quantity of wolframite, it was observed that the mother liquors from the ammonium paratungstate had

a dark colour. This colour was found to be due to the presence of *ammonium vanadichosphotungstate*,  $(\text{NH}_4)_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5 \cdot \text{WO}_3 \cdot x\text{H}_2\text{O}$ , which forms large, brilliant, black, octahedral crystals. E. G.

**Preparation of Antimony Hydride.** By ALFRED STOCK and WALTHER DOHT (*Ber.*, 1902, 35, 2270—2275).—Alloys of antimony and zinc give a very poor yield of the hydride; a gas containing 0.71 per cent. of the hydride by volume can be obtained by the action of 12 per cent. hydrochloric acid on an alloy containing 40 per cent. of antimony, and a gas containing 0.96 per cent. of antimony hydride by the action of dilute sulphuric acid on a 25 per cent. alloy. The sodium alloys give even smaller yields. Antimony-calcium alloys, when decomposed with dilute hydrochloric acid in a freezing mixture, give a gas containing up to 16.3 per cent. of the hydride, but the total yield of gas is small. The best results are obtained with alloys of antimony and magnesium; an alloy containing 33 per cent. of antimony decomposed with 12 per cent. hydrochloric acid in a freezing mixture gives a gas containing 10.4—14.0 per cent. of antimony hydride. The remainder of the gas, if carefully dried, consists of pure hydrogen, and on cooling with liquid air, the antimony hydride separates in a pure condition. It melts at  $-88^\circ$  to a water-white liquid, boils at  $-17^\circ$  under 760 mm. pressure, leaving no residue, and gives a gas consisting entirely of the hydride  $\text{SbH}_3$ . In a pure state, the gas only begins to deposit antimony after some hours at the atmospheric temperature, but rapidly decomposes above  $150^\circ$ . Olszewski (*Abstr.*, 1886, 977), who states that the gas begins to decompose at  $-60^\circ$ , was probably dealing with an impure or moist gas. T. M. L.

**Kermes Mineral.** By KARL FEIST (*Arch. Pharm.*, 1902, 240, 241—244).—The crystalline constituent of kermes mineral, hitherto regarded as antimony oxide, is shown to be sodium pyroantimonate,  $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$ . It is present when the kermes is prepared by boiling antimony sulphide with 10 per cent. aqueous sodium carbonate, the air having access; in the absence of air, the preparation has no crystalline constituent. The analogous potassium compound is much more soluble, and does not crystallise so easily; in consequence, kermes mineral, prepared by means of potassium, instead of sodium, carbonate, contains little or no antimonate. C. F. B.

**Isomorphism of Salts of Bismuth and some of the Rare Earths.** By GÖSTE BODMAN (*Zeit. Kryst. Min.*, 1902, 36, 192—193; from *Bihang K. Svenska Vet. Akad. Handl.*, 1900, 26, II, No. 3. Compare *Abstr.*, 1898, ii, 435).—Mixed crystals of didymium and bismuth nitrate belong to two types. Those of one series are of a deep red colour with  $\text{Di}:\text{Bi}=4:1$  to  $1:1$ , and the formula  $(\text{Di,Bi})(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ; sp. gr. = 2.296—2.480. Those of the other series are of a faint amethyst-red, with  $\text{Di}:\text{Bi}$  less than  $1:4$ , and only  $5\text{H}_2\text{O}$ ; sp. gr. = 2.700—2.813.

Mixed crystals of bismuth and lanthanum also belong to two types. In one series, with  $\text{Bi}:\text{La}=55:1$  to  $12.6:1$ , the sp. gr. and the amount of water are the same as in bismuth nitrate; another mixture, with

La : Bi = 67 : 1, has  $6\text{H}_2\text{O}$  and sp. gr. = 2·367. Crystals of bismuth and yttrium nitrate are also of two types, with sp. gr. = 2·816—2·653 and 2·286—2·152.

Only sulphates containing small amounts of bismuth were obtained, as given below :

	Di : Bi.	Sp. gr.
$(\text{Di}, \text{Bi})_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ .....	2—49 : 1	2·85—3·067
$(\text{La}, \text{Bi})_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ .....	7·4—149 : 1	2·870—2·847
$(\text{La}, \text{Bi})_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ .....	9·37—210 : 1	3·148—3·105
$(\text{Y}, \text{Bi})_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ .....	6·15—139 : 1	2·551—2·651

L. J. S.

**Radioactive Bismuth-Polonium.** By WILHELM MARCKWALD (*Ber.*, 1902, 35, 2285—2288).—The presence of some new element, polonium, in ordinary radioactive bismuth has been established. When a solution of the chloride is electrolysed, the metal which is first deposited is much more radioactive than the original substance, and even when a polished rod of bismuth is placed in a solution of the chloride a small, extremely active, metallic deposit is formed on the surface of the bismuth, owing to the difference in potential between the new element and metallic bismuth. After three days, the whole of the active element has become deposited, and the solution shows no radioactivity. The deposit contains small amounts of chloride, which can be removed by sublimation ; the metallic bead thus obtained dissolves in nitric acid, and the solution exhibits most of the reactions characteristic of bismuth ions. The active rays emitted by the metal and its solutions differ from radium rays, as they are incapable of passing through paper and other obstacles. The author hopes to obtain sufficient of the new metal to determine its atomic weight. The activity of the specimens of polonium does not diminish even after several months.

J. J. S.

**Colloidal Gold.** By CARL PAAL (*Ber.*, 1902, 35, 2236—2244).—On mixing an alkaline solution of protalbic or lysalbic acid and a solution of gold chloride, a clear, pale yellow solution is obtained, which contains gold in the ordinary condition, as it can be dialysed and gives the ordinary reactions. On warming this solution or treating it with formaldehyde, &c., it becomes ruby-red in colour, and now contains colloidal gold, which is no longer capable of passing through a dialyser. When the solution is poured into alcohol or cautiously acidified, a coloured solid is thrown down which may contain 90 per cent. of colloidal gold. This solid is soluble in dilute alkali, is of metallic appearance, resembling iron pyrites, and has a high specific gravity.

K. J. P. O.



## Mineralogical Chemistry.

**Composition of Silver Amalgam from Sala.** By HJALMAR SJÖGREN (*Zeit. Kryst. Min.*, 1902, 36, 192; from *Geol. För. Förh.*, 1900, 22, 187—190).—Two varieties of silver amalgam occur at Sala in Sweden, of which the following analyses by R. Mauzelius are given. I, Crystals the size of a pea or bean rich in faces are found in cavities filled with mercury. The mineral is of a brilliant silver-white colour; it is brittle and has a conchoidal fracture. II, Impure massive material filling crevices; this tarnishes yellow, has a hackly fracture, and is only slightly brittle:

	Ag.	Hg.	Cu.	Zn.	Fe.	S.	Insol. (silicate)	Total.	Sp. gr.	Formula.
I.	26.48	73.44	—	—	—	—	—	99.92	13.71	Ag <sub>3</sub> Hg <sub>3</sub>
II.	27.25	63.86	1.38	1.37	1.97	[3.21]	0.96	100.00	11.56	Ag <sub>5</sub> Hg <sub>6</sub>
										L. J. S.

**Ferghana Naphtha.** By K. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 395—397).—The author has examined naphtha from Liakan in the Province of Ferghana. It yields about 23.8 per cent. of kerosine, 2.6 of paraffin, and practically no 'benzine'; the percentage of sulphur is 0.57.

T. H. P.

**Discovery of Gold Tellurides in Western Australia.** By ARTHUR G. HOLROYD (*Trans. Australian Inst. Mining Eng.*, 1897, 4, 186—193).—The important discovery of tellurides of gold at Kalgoorlie in the East Coolgardie gold-field was announced by the author in *The Kalgoorlie Miner* of May 29th, 1896. The mineral species recognised are calaverite and sylvanite; native tellurium is also recorded. Analyses of the calaverite gave:

Au.	Ag.	Te.
44	traces	55
39.2	3	54

The gold set free by the oxidation of the tellurides is amorphous ("mustard-gold") or finely crystallised ("sponge-gold"). L. J. S.

[**Calaverite and Coloradoite from Western Australia.**] By EDWARD S. SIMPSON (*Ann. Prog. Rep. Geol. Survey, Western Australia* for 1897, 1898, 46—50).—Calaverite from several mines at Boulder [Kalgoorlie] is massive and has a pale brass-yellow colour. Some specimens are described as having a perfect cleavage in one direction [these are probably sylvanite.—L. J. S.], whilst others have an uneven to sub-conchoidal fracture. Analyses (II by G. J. Rogers) gave results agreeing with the formula AuTe<sub>2</sub>. Other specimens contained 41.28 and 37.10 per cent. of gold:

	Te.	Au.	Ag.	S.	Cu.	Fe.	Pb, Bi, Zn.	Total.	Sp. gr.
I.	57.27	41.37	0.58	—	—	—	—	99.22	9.311
II.	59.69	38.70	1.66	0.09	0.21	0.18	traces	100.53	—

The telluride of mercury, coloradoite, is recorded from this locality.

It is massive with a conchoidal fracture, dark lead-grey colour and brilliant metallic lustre; sp. gr. 9.21. It is associated with free gold, cinnabar, calaverite and small rhombic crystals of another telluride of gold, perhaps krennerite. L. J. S.

[Coloradoite from Western Australia.] By EDWARD S. SIMPSON (*Ann. Prog. Rep. Geol. Survey, Western Australia* for 1898, 1899, 57—59).—Analysis of material from Boulder similar to that before described (compare preceding abstract) gave:

Hg.	Ag.	Au.	Te.	Total.
50.40	0.12	trace	[49.48]	100.00

From these results, the formula  $\text{Hg}_2\text{Te}_3$  is deduced. The formula at present accepted for this mineral, namely,  $\text{HgTe}$ , is based on Genth's analyses of material from Colorado which showed 2.9—46.8 per cent. of impurities; it is pointed out that the mean of these analyses agrees better with the new formula than with the old. L. J. S.

Zincite from Poland. By J. A. ANTIPOFF (*Zeit. Kryst. Min.*, 1902, 36, 176; from *Verh. k. russ. min. Ges.*, 1900, 38, prot. 41—42).—A mineral, thought to be calamine, from the Olkuschsk mine is shown by the following analysis and the crystalline form to be zincite, a mineral now recognised for the first time as occurring in Russia:

ZnO.	PbO.	CO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Insol.	Organic matter.	Total.
91.47	5.26	2.85	0.11	0.12	trace	99.81.

This corresponds with ZnO, 88.25;  $\text{PbCO}_3$ , 6.41;  $\text{ZnCO}_3$ , 5.03 per cent. L. J. S.

A Uranium Mineral Resembling Voglite. By J. A. ANTIPOFF (*Zeit. Kryst. Min.*, 1902, 36, 175; from *Verh. K. russ. min. Ges.*, 1900, 38, prot. 38—41).—The mineral is found as fine scales on, and embedded in, calcite at the Utsch-Kirtan pass, 120 kilometres from Margelan in Gov. Ferghana. It appears to be isotropic; sp. gr. 3.35. Analysis of isolated scales gave the results under I; neglecting iron and calcium, this gives the formula  $(\text{CO}_3)_2(\text{UO}_2)\text{Cu}, 10\text{H}_2\text{O}$ , near to that of the Bohemian voglite. Analysis of the calcite with the enclosed mineral gave II; here the ratio of  $\text{U}_2\text{O}_3$ :CuO is different from that in analysis I:

	H <sub>2</sub> O.	CO <sub>2</sub> .	U <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CuO.	CaO.	P <sub>2</sub> O <sub>5</sub> .	SiO <sub>2</sub> .	Total.
I.	42.13	10.88	35.45	1.12	9.71	1.35	trace	—	100.64
II.	4.83	32.35	11.72	4.22	3.41	40.12	0.54	3.18	100.37
III.	—	—	78.25	12.09	8.41	—	—	—	98.75

When the mineral is treated with hydrochloric acid, small, yellowish-green scales remain; this insoluble residue has the composition given under III, corresponding with the formula  $\text{U}_2\text{O}_3, \text{CuO}$ . Such a compound has not before been observed in nature, but has been prepared by Debray. L. J. S.

Separation of Glauber Salt [Mirabilite] in the Kara-bugas. By NICOLAI S. KURNAKOFF (*Zeit. Kryst. Min.*, 1902, 36, 174—175; from *Verh. K. russ. min. Ges.*, 1900, 38, prot. 26—27. Compare Abstr.,

1899, ii, 303).—The solubility relations of glauber salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) are as follows. In pure water, 5.02 per cent. at  $0^\circ$  and 16.8 per cent. at  $17.9^\circ$ ; in water containing 10 parts of sodium chloride, 4 per cent. at  $0^\circ$  and 14 per cent. at  $17.9^\circ$ . A saturated solution of sodium chloride and glauber salt contains:

	$\text{Na}_2\text{SO}_4$ .	$\text{NaCl}$ .
At $0^\circ$ .....	1.77	32.85 per cent.
„ $17.9^\circ$ .....	11.10	33.22 „

Analysis of the water of the Kara-bugas Gulf of the Caspian Sea gave:

$\text{NaCl}$ .	$\text{Na}_2\text{SO}_4$ .	$\text{MgCl}_2$ .	$\text{CaSO}_4$ .
10.55	4.80	5.30	0.45

On comparing these results with the solubilities given above, it will be seen that in summer, when the mean temperature is  $18$ – $20^\circ$ , the water is not saturated with salts, but that in winter (mean temp.  $3$ – $5^\circ$ ) glauber salt will separate. At no time of the year is the water saturated with sodium chloride, so that the glauber salt separates out alone.

L. J. S.

**Scheelite from Maderanerthal, Switzerland.** By CARL SCHMIDT (*Zeit. Kryst. Min.*, 1902, 36, 160–161).—The second crystal of scheelite that has been found in the Maderanerthal is described. It is an isolated, colourless, and transparent crystal measuring 3.5 cm. in length. The angle  $(111):(11\bar{1})$  is  $49^\circ 27'$ . Analysis by Hinden gave:

$\text{CaO}$ .	$\text{MoO}_3$ .	$\text{WO}_3$ .	Total.
19.45	0.49	79.53	99.47

No connection can be traced between the small variations in the angles of scheelite and the amount of molybdenum present.

L. J. S.

**Hydrated Aluminium Silicates.** By KONSTANTIN D. GLINKA (*Zeit. Kryst. Min.*, 1902, 36, 188–189; from *Verh. russ. min. Ges.*, 1900, 37, 311–332. Compare Abstr., 1900, ii, 89).—The precipitate obtained when halloysite or kaolin is treated with potassium hydroxide and the solution neutralised with hydrochloric acid has the composition  $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ . A precipitate having the same composition is also obtained when gibbsite is treated with potassium hydroxide, mixed with a solution of silica in potassium hydroxide, and the mixture acidified.

L. J. S.

**Analcite in Liassic Clay from Lehre.** By JOHANNES FROMME (*Jahresber. Ver. Naturwiss. Braunschweig*, 1902, 13, 5 pp.).—Small crystals of analcite with the forms  $n\{211\}$  and  $a\{100\}$  occur, together with blende, marcasite, dolomite, calcite, barytes and gypsum, in geodes in Liassic clay at Lehre, near Brunswick. The minerals have been formed in the order just named, and the sulphates have been derived by the oxidation of the sulphides. Analysis I is of crystals of analcite isolated from the carbonates by the action of a 10 per cent. solution of hydrochloric acid; by the action of the acid, the crystals have been decomposed on the surface and coated with a film of silica, and this partly explains the excess of silica shown in the analysis.

Other crystals not treated in this manner gave the partial results under II; the excess of silica is here due to quartz grains enclosed in the crystals, which remain as a gritty residue when the crystals are decomposed by a 38 per cent. solution of hydrochloric acid.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	58.59	20.61	0.48	0.40	0.04	0.98	11.02	8.26	100.38
II.	57.20	21.71	—	—	—	—	—	—	—
III.	54.35	21.92	0.57	1.42	—	0.28	12.54	9.17	100.25

Analysis III (by Ohlmer) is of analcite from Frombach. L. J. S.

**Ilvaite from Siorarsuit, Greenland.** By O. B. BÖGGILD (*Meddelelser om Grønland*, 1902, 25, 43—89).—A crystallographic description, illustrated with thirty-two figures, is given of the brilliant black crystals of ilvaite which occur somewhat abundantly in augite-syenite, sodalite-syenite, and foyaite at Siorarsuit, near Julianehaab, in South Greenland. The natural and artificially produced etch-figures conform with orthorhombic symmetry. The strong pleochroism may even be observed in the light reflected from the surface of the crystals. Sp. gr. 4.0065. Analysis by C. Christensen gave the following results, agreeing with the usual formula,  $\text{HCaFe}''_2\text{Fe}'''\text{Si}_2\text{O}_9$ .

SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	H <sub>2</sub> O.	Total.
29.62	19.48	33.28	2.20	14.38	2.24	101.20

The following table compares the variation in the axial ratios with the amount of manganese present:

	MnO per cent.	$a:b:c$ .
Elba .....	0.74—1.55	0.6665:1:0.4427
Kangerdluarsuk.....	1.97	0.6744:1:0.4484
Siorarsuit .....	2.20	0.6766:1:0.4499
Herbornseelbach .....	6.78—8.68	0.6795:1:0.4576

L. J. S.

**Brunsvigite, a new Leptochlorite from the Radauthal.** By JOHANNES FROMME (*Tsch. Min. Mitth.*, 1902, 21, 171—177).—A chloritic mineral of wide distribution in the gabbro of the Radauthal, Harz, is described under the new name *brunsvigite*. It occurs as cryptocrystalline and fine scaly masses in veins of quartz, calcite and various mineral sulphides, in which it fills crevices or forms small, radially fibrous aggregates. It is green to dark leek-green, and optically uniaxial and negative; the hexagonal scales have a perfect cleavage parallel to the basal plane. Sp. gr. = 3.01. The following analysis gives the formula  $6\text{SiO}_2, 2\text{Al}_2\text{O}_3, 6\text{FeO}, 3\text{MgO}, 8\text{H}_2\text{O}$ , which is written, in accordance with Tschermak's theory of the chlorites, as  $\text{Sp}_5\text{At}_3\text{At}'_2$ , or  $5(\text{Si}_2\text{Mg}_3\text{H}_4\text{O}_9), 3(\text{SiAl}_2\text{Mg}_2\text{H}_4\text{O}_9), 2(\text{SiAl}_2\text{MgH}_4\text{O}_8)$ . The mineral is most closely related to metachlorite, which it closely resembles in appearance and sp. gr.

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	H <sub>2</sub> O.	Moisture.	Total.
27.88	15.81	1.77	31.92	0.51	0.20	9.52	11.97	0.15	99.73

L. J. S.

**Composition of Water in Salt-lakes in the Crimea.** By NICOLAI S. KURNAKOFF (*Zeit. Kryst. Min.*, 1902, 36, 174; from *Verh. K. russ. min. Ges.*, 1900, 38, prot. 24—26).—The author has previously shown that the ratio of  $\text{MgSO}_4 : \text{MgCl}_2$  in the waters of many marine salt-lakes in the Crimea is always 0·5—0·7. In salt-lakes which receive part of their water from continental areas, this ratio is less, and in typical continental salt-lakes it is very nearly zero. Analyses of the water of different salt-lakes of the Perekop group gave the percentages under I—III. Water (anal. IV) from the Genitschesk salt-lake, which is situated near the sea, is also of the same character, and is therefore largely collected from a continental area :

	$\text{CaSO}_4$ .	$\text{CaCl}_2$ .	$\text{MgSO}_4$ .	$\text{MgCl}_2$ .	$\text{NaCl}$ .	$\text{MgSO}_4 : \text{MgCl}_2$ .
I.	0·05	1·98	—	18·27	8·01 per cent.	0
II.	0·05	—	1·95	7·33	24·33 „	0·266
III.	0·13	1·39	—	10·26	12·80 „	0
IV.	0·05	—	3·21	9·21	14·34 „	0·349

L. J. S.

**Volcanic Dust which fell on Barbados after the St. Vincent Eruption.** By JOHN SMITH FLETT (*Abstr. Proc. Geol. Soc.*, 1902, 117).—The dust which fell on Barbados on May 7th, 1902, after the volcanic eruption at St. Vincent, is a fine, grey, gritty powder, all of which passes through a sieve with 30 meshes to the inch. It contains plagioclase-felspar (generally idiomorphic labradorite) coated with a thin film of glass, hypersthene, brownish monoclinic augite, both frequently in perfect crystals, magnetite, apatite, possibly zircon, and fragments of a brown glass. Analysis by W. Pollard gave :

$\text{SiO}_2$ .	$\text{TiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{MnO}$ .	$(\text{CoNi})\text{O}$ .	$\text{CaO}$ .
52·81	0·95	18·79	3·28	4·58	0·28	0·07	9·58
$\text{MgO}$ .	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	$\text{P}_2\text{O}_5$ .	$\text{SO}_3$ .	$\text{Cl}$ .	$\text{H}_2\text{O}$ .	Total.
5·19	0·60	3·23	0·15	0·33	0·14	0·37	100·35

L. J. S.

## Physiological Chemistry.

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**Metabolism and Diet.** By FRANCIS W. GOODBODY, NOEL D. BARDSWELL, and J. E. CHAPMAN (*J. Physiol.*, 1902, 28, 257—273).—Forced feeding in the healthy subject causes marked deterioration in health, and the bad effects last a long time. There is a marked increase in the total urinary nitrogen, but the proportion of urea remains normal. The amount of nitrogen retained is small, but the inorganic constituents of the urine increase. In the fæces, the amount of fat is increased, but not the nitrogen. W. D. H.

**Metabolism in Men with Special Reference to Proteid Requirements.** By V. O. SIVEN (*Bied. Centr.*, 1902, 31, 351—352; from *Scand. Arch. Physiol.*, 11, 308).—In an experiment made by the author on himself in which the amount of nitrogen consumed,

commencing with a normal diet, was reduced as much as possible while maintaining equilibrium, a minimum, of 4 grams was reached with food equivalent to 2747 Cal. (43 Cal. per kilo.). The experiment is not quite conclusive, as it lasted only four days, but the limit as indicated is probably approximately correct.

On increasing the amount of nitrogen to 22.6 grams, it was only during the first day or two that any considerable portion of it was retained.

Determinations of sulphur and phosphorus in the food and excrement showed that the changes in these substances follow those of nitrogen.

N. H. J. M.

**Rôle of Crude Fibre in the Nitrogenous Metabolism of the Animal Organism.** By W. USTJANTZEW (*Landw. Versuchs-Stat.*, 1902, 56, 463—475).—Two sheep were fed for three periods of 6 or 7 days with (1) 400 grams of beans, (2) 354 grams of beans and 310 grams of hay, and (3) 300 grams of beans and 353 grams of hay. The nitrogen digested was about the same in each case (16.04, 16.93, and 15.73 grams), whilst the amounts of digested crude fibre and non-nitrogenous extract were 24.14, 87.39, and 132.74 grams, and 163.54, 224.54, and 259.09 grams respectively. The nitrogen in the urine amounted, in the three periods, to 16.51, 15.60, and 12.88 grams per head per day.

The experiment was then continued for two further periods, in which the sheep received (4) 380 grams of beans and 140 grams of rice and (5) 400 grams of beans and 100 grams of sugar. The amount of nitrogen digested again remained the same, whilst the amount of crude fibre digested was about the same as in the first period. As regards non-nitrogenous extract, the amounts digested in periods (4) and (5) were about the same as in (3). The amount of nitrogen in the urine in (4) and (5) was lower than in (1) but higher than in (3).

Experiments made with a rabbit are also described. Whilst starch and sugar effect an economy of proteids in the animal organism, crude fibre possesses this power in a very limited degree. N. H. J. M.

**Physiological Value of Meat.** By JOHANNES FRENZEL and M. SCHREUER (*Bied. Centr.*, 1902, 31, 391—394; from *Arch. Anat. Physiol.*, 1901, 284—298 and 499—512).—The experiment was made with a dog fed with 470 grams of chopped beef and 130 grams of meat meal (free from fat) per day and lasted five days. Before the commencement of the experiment, the bladder was emptied and carefully rinsed out with 3 per cent. boric acid solution. The following results were obtained.

1 gram of beef, free from fat and mineral matter, = 5629.25 cal.,  
1 gram of nitrogen in urine and in faeces (free from fat) = 7.31, and  
48.24 Cal. respectively. Value for 1 gram of nitrogen in meat meal  
= 25.62 Cal. Physiological value of the meat and meat-meal diet  
= 74.84 per cent. N. H. J. M.

**Physiological Value of Meat Extract.** By JOHANNES FRENZEL and N. TORIYAMA (*Bied. Centr.*, 1902, 31, 391—395; from *Arch. Anat. Physiol.*, 1901, 284—289 and 491—512).—The experiment was similar

to that of Frenzel and Schreuer (preceding abstract). In the preliminary period, the dog received potato starch (100 grams), lard (50 grams), and meat ash (3 grams) per day. In the experimental period, 500 c.c. of a solution of meat extract was given each day in two portions. During this period, the dog received 815.05 Cal., and during the four days' experiment 3260.20 Cal. per day.

Comparing the results of the experimental period with those obtained in the preliminary period, it is found that addition of meat extract to the food resulted in an increased separation of nitrogen in urine and faeces and an increase in the heat values of the excrementitious matters. The conclusion is drawn, in agreement with Pflüger but in opposition to Rubner, that the non-proteid extract of meat has a very considerable share (about two-thirds) in the metabolism.

N. H. J. M.

**The End Products of Gastric Digestion. II.** By LEO LANGSTEIN (*Beitr. chem. Physiol. Path.*, 1902, 2, 229—237).—After gastric digestion had been allowed to go on for three months on crystallised egg-albumin, saturation with ammonium sulphate gave no precipitate, but the biuret reaction was still given. The difference between peptic and tryptic digestion is regarded as mainly quantitative; the persistence of the biuret reaction is one important difference; the absence of histidine and arginine among the products is another. The substances isolated were leucine, tyrosine, glutamic and aspartic acids, cystin, lysine (in small amount), pentamethylenediamine, hydroxyphenylethylamine, and "a polymeric carbohydrate containing nitrogen." Further, a base yielding scatole and two acids of uncertain nature were found. These acids differ by their solubilities in alcohol; they give the biuret reaction, but no other proteid reactions.

W. D. H.

**Synthetic Action on Dextrose with Pancreatic Ferment.** By A. CROFT HILL (*Proc. Physiol. Soc.*, 1902; *J. Physiol.*, 28, xxvi—xxvii).—The reversible action previously described with other diastatic ferments also occurs with pancreatic ferment. The importance of such observations in explaining intracellular syntheses in plants and animals is pointed out.

W. D. H.

**Human Intestinal Juice.** By HARTOG J. HAMBURGER and E. HEKMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 4, 733—746).—The observers had the unusual opportunity of examining human succus entericus. For surgical reasons, it became necessary to isolate a loop of the small intestine, and this loop continued to discharge intestinal juice to the exterior for some time after the operation. This juice, like that of the dog, contains a substance which renders pancreatic juice active. It does not exercise any energising influence on the fat-splitting and amylolytic ferments of the pancreas, but its action on the tryptic ferment is most marked. Quantitative experiments do not bear out Pawloff's view that the active substance in the intestinal juice is a ferment, for it is not able, like a ferment, to act on an unlimited amount of pancreatic juice. The name *zymolysin* is suggested as more appropriate than enterokinase, because its action



appears to be that of liberating the enzyme (trypsin) from its zymogen (trypsinogen).

Some experiments regarding the rate of secretion of the juice are recorded, but although work in this direction is necessarily incomplete, the results obtained show that as in the case of the other digestive juices, the amount is proportional to the necessities of the digestive process.

Cohnheim's erepsin is also present in the human juice; it is not identical with zymolysin, because erepsin is destroyed by heating the juice to 59° for three hours; zymolysin is not destroyed until the temperature is raised to 67°.

W. D. H.

**Absorption of Simple Stereoisomeric Sugars in the Small Intestine.** By JUNZO NAGANO (*Pflüger's Archiv*, 1902, 90, 389—404).—The experiments were made on dogs with a Vella's fistula. The amount of stereoisomeric sugars absorbed is different. Typical results are given in the following table:

Sugar.	Strength of solution.	Amount absorbed.
<i>d</i> -Galactose .....	5 per cent.	all
	7.5 "	83 per cent.
Dextrose .....	5 "	all
	6 "	75 "
	7.5 "	69 "
<i>d</i> -Mannose .....	1 "	all
	2.5 "	71 "
	5 "	56—59 "
<i>d</i> -Fructose .....	2.5 "	all
	5 "	88 "
	7.5 "	60 "

Pentoses are less absorbed than hexoses, and show also individual differences. In the upper part of the intestine, sugar is absorbed more rapidly than water; in the lower part, it is the reverse. W. D. H.

**The Formation of *iso*Valeraldehyde and Acetone from Gelatin.** By CARL NEUBERG and FERDINAND BLUMENTHAL (*Beitr., chem. Physiol. Path.*, 1902, 2, 238—250).—The origin of acetone in the body is a moot point. Whether it always has the same origin is doubtful. The views that it comes from fat, from carbohydrate, or from intestinal putrefaction of proteids are discussed and largely dismissed. The view considered to be most tenable is that it originates by the oxidation of proteid material. The present experiments with gelatin show that acetone is formed as a result of oxidation in the laboratory. Another volatile substance separated out was *isovaleraldehyde*. The possible way in which such substances might originate is discussed.

W. D. H.

**Ammonia in the Blood and Organs of the Dog.** By W. HORODYŃSKI, SERGEI SALASKIN, and J. ZALESKI (*Zeit. physiol. Chem.*, 1902, 35, 246—263).—The amount of ammonia in dog's arterial blood

is very constant (average 0.41 mg. per 100 grams of blood; in hunger 0.42; after administration of ammonium salts 0.42). In the portal blood, it is from 3 to 5 times greater. In animals with an Eck's fistula, the amount of ammonia increases. The auto-intoxication in such animals is due to acid products, not to the ammonia. The amount of ammonia in such organs as the brain is fairly constant; in organs the activity of which varies, like secreting glands, it is variable. It increases in the brain when an Eck's fistula is made. It increases in the tissues and organs (except the brain) during hunger, indicating proteid katabolism. Some of the conclusions arrived at by Biedl and Winterberg (this vol., ii, 157) are criticised. W. D. H.

**Iron in Human Liver Cells.** By P. BIELFELD (*Beitr. chem. Physiol. Path.*, 1902, 2, 251—260).—The amount of iron in the normal liver cells of women (0.05 to 0.09 per cent.) is usually less than, and varies within narrower limits than that in, the liver cells of men (0.05 to 0.36). In reference to age, the amount is least at from 20—25 years, and is then about the same in the two sexes. W. D. H.

**Acid Formation in Autolysis of the Liver.** By ADOLF MAGNUS-LEVY (*Beitr. chem. Physiol. Path.*, 1902, 2, 261—296).—In the liver of various animals subjected to autolysis, the following non-volatile acids were separated, fermentation lactic acid, *d*-lactic acid, and succinic acid; the volatile acids include formic, acetic, butyric, and a higher acid in small quantities; the gases are hydrogen sulphide, hydrogen, and carbon dioxide. This occurs whether the autolysis be conducted antiseptically or aseptically. The presence of antiseptics lessens the amounts of succinic and butyric acids. Acid formation is attributed to ferment action. The possibility of a similar action during life will help to explain the increased formation of acid in certain pathological conditions such as fever, diabetes, and phosphorus poisoning. The auto-digested liver is strongly reducing; urobilin is also formed in considerable amount, but whether from bilirubin or hæmoglobin is uncertain. W. D. H.

**Reticulin and Collagen.** By MAX SIEGFRIED (*J. Physiol.*, 1902, 28, 319—324).—Polemical against Miss Tebb (this vol., ii, 218). The existence of reticulin as a chemical entity is still maintained. W. D. H.

**The Presence of Arsenic in Normal Animal Organs.** By ARMAND GAUTIER (*Compt. rend.*, 1902, 134, 1394—1399). By GABRIEL BERTRAND (*ibid.*, 1434—1437).—Fresh experimental evidence is given in favour of Gautier's statement that arsenic is a normal constituent of many animal tissues and organs. W. D. H.

**The Production of Dextrose by Muscles.** By CADÉAC and MAIGNON (*Compt. rend.*, 1902, 134, 1443—1445. Compare this vol., ii, 466).—Muscles produce sugar after death, as does the liver. If they are plunged into oil at 37°, the same amount of sugar is produced as in the muscles kept at the same temperature in the air. If they are sur-

rounded by ice, only a small amount of sugar is formed. If they are crushed, the maximum of sugar is produced. This function is independent of putrefaction.

W. D. H.

**Adrenalin.** By T. B. ALDRICH (*Amer. J. Physiol.*, 1902, 7, 359—368).—Evidence is brought forward to show that adrenalin is the reducing and blood-pressure-raising substance found in the suprarenal gland, and is not a modified or changed form of the active substance as Abel contends. Epinephrin and other "questionable" products are regarded as oxidised or changed forms of the active principle since they do not reduce Fehling's solution.

W. D. H.

**Osseo-albumoid and Chondro-albumoid.** By P. B. HAWK and WILLIAM J. GIES (*Amer. J. Physiol.*, 1902, 7, 340—358. Compare this vol., ii, 408).—The albumoid obtainable from bone after hydration of the collagen, is the substance previously described by Broesicke as keratin. It is not keratin or typical elastin, although it somewhat resembles elastin. Its percentage composition is C, 50.16; H, 7.03; N, 16.17; S, 1.18; O, 25.46. It contains no phosphorus. Chondro-albumoid, previously described by Möerner, is also free from organic phosphorus; its percentage composition is C, 50.46; H, 7.05; N, 14.95; S, 1.86; O, 25.68.

W. D. H.

**Cerebrospinal Fluid.** By EMIL ZDAREK (*Zeit. physiol. Chem.*, 1902, 35, 201—204).—The specimen of cerebrospinal fluid examined was obtained from a meningocele occurring in a woman. 370 c.c. of clear fluid were obtained, of a light yellow colour, faintly alkaline reaction, and sp. gr. 1.0018. It reduced Fehling's solution and gave characteristic crystals of phenylglucosazone. It contained neither lecithin nor cholesterol. The following table gives the results of analysis in parts per 1000:

Dry residue .....	10.452
Organic substances.....	2.096
Proteid .....	0.768
Substances soluble in ether.....	0.358
Ash soluble in water .....	8.220
Ash insoluble in water .....	0.168

The soluble ash consisted of  $\text{SO}_3$ , 0.048; Cl, 4.245;  $\text{CO}_2$ , 0.498;  $\text{K}_2\text{O}$ , 0.167;  $\text{Na}_2\text{O}$ , 4.294; less O = Cl, 0.958; total, 8.294.

W. D. H.

**Specific Heat of Milk.** By WILHELM FLEISCHMANN (*J. Landw.*, 1902, 50, 33—76).—The results of new determinations show that the specific heats of cream, milk, and skim milk are 0.8494, 0.9407, and 0.9512 respectively. The specific heat increases slightly with the percentage of fat, and it also increases with the age of the milk.

In reference to the statement in his *Lehrbuch d. Milchwirtschaft* (1891, 36) that the fat of milk and cream is probably in a fluid state, the author now considers that when milk is kept at the ordinary

temperature (12—20°) or at lower temperatures, the fat readily solidifies.  
N. H. J. M.

**The Film on Heated Milk.** By LEO F. RETTGER (*Amer. J. Physiol.*, 1902, 7, 325—330).—The formation of a film or skin on heated milk is dependent on the presence of proteid. This proteid is caseinogen. The presence of fat facilitates film formation, but is not essential. Whilst surface evaporation facilitates film production, it is not necessary (compare Jamison and Hertz, *Abstr.*, 1901, ii, 672).  
W. D. H.

**Hæmolytic Action of Venin.** By A. CALMETTE (*Compt. rend.*, 1902, 134, 1446—1447).—The venin of snakes, especially of the cobra, hæmolyses the red corpuscles of the horse, dog, rabbit, guinea-pig, and rat rapidly; those of the ox, fowl, pigeon, and frog are more resistant. Flexner and Noguchi (*J. exp. Med.*, 1902, March 17) state that if the corpuscles are freed from serum by salt solution and centrifugalisation, they are no longer hæmolysed by venin, but that they dissolve perfectly when restored to their original serum. They conclude that the alexine of the serum is essential for the solution of the corpuscles. In the present research, on the contrary, it is found that the normal serum has anti-hæmolytic power, which is destroyed at 56°. Venin can be heated to 75° without losing its properties. The washed corpuscles are able to fix the venin, and when transferred to serum which has previously been heated at 62°, they rapidly dissolve.  
W. D. H.

**Physiological Action of Extracts of Animal Tissues.** By SWALE VINCENT and WILLIAM SHEEN (*Proc. Physiol. Soc.*, 1902; *J. Physiol.*, 23, xix—xxi).—Saline decoctions of nervous tissues, muscle, testis, kidney, spleen, pancreas, liver, stomach, intestine, lung, and mammary gland, all produce a fall of blood-pressure when intravascularly injected. Whether the depressor substance is the same throughout is uncertain. Suprarenal medulla and the infundibular portion of the pituitary body are the only tissues which yield a pressor substance. The latter contains also a depressor substance, probably of the same nature as that obtained from nervous tissues generally. The depressor substance in muscle and nervous tissues can be extracted by alcohol, but not by ether. Its action is not counteracted by atropine.  
W. D. H.

**Intestinal Calculi.** By GUSTAVE PATEIN and R. BROUANT (*J. Pharm. Chim.*, 1902, [vi], 15, 509—512).—Three intestinal calculi excreted by a patient had the following percentage composition, water 11·95, organic matter 2·00, magnesium phosphate 10·95, calcium phosphate 6·14, calcium carbonate 52·66, and sulphur 16·30. The last, a quite unusual constituent of such secretions, is supposed to have originated by the medicinal employment of the substance by the patient. A case of rectal secretion of sulphur mixed with magnesium oxide originating in this manner is also quoted.  
T. A. H.

**Excretion of Indoxyl, Phenol, and Glycuronic Acid in Phloridzin Diabetes.** By PAUL MAYER (*Beitr. chem. Physiol. Path.*, 1902, 2, 217—228).—In phloridzin diabetes, no glycuronic acid passes into the urine, nor is there any increase in the excretion of phenol or indoxyl. There is no relationship between the excretion of indoxyl and phenol and that of glycuronic acid. If the excretion of this acid is increased by well-known methods, that of the aromatic substances mentioned does not rise; this conflicts with the statements made by Lewin (this vol., ii, 272).  
W. D. H.

**Lymphagogue Action of the Strawberry.** By LAFAYETTE B. MENDEL and DONALD R. HOOKER (*Amer. J. Physiol.*, 1902, 7, 380—386).—It is well known that eating certain fruits, especially strawberries, produces in a few susceptible people an urticaria comparable to that produced by eating shell-fish. This led to the question whether it is a lymphagogue. Clopatt (*Skand. Arch. Physiol.*, 1900, 10, 403) found that it was, and the present experiments on dogs confirm his conclusion. The action cannot be explained by the small amount of sugar and salt in the fruit. An aqueous extract of strawberries injected intravenously produces an increased flow from the thoracic duct, a fall of blood pressure, and a lessening of the coagulability of the blood. These effects are most marked with the first injection. There is little or no diuretic action. These facts place strawberry extract among Heidenhain's first class of lymphagogues. The lymph was observed to flow after the animal's death, and this emphasises the importance of living or "surviving" cells as a factor in lymph formation.  
W. D. H.

**Method of Characterising Physiological and Pathological Proteids.** By GUSTAVE PATEIN (*J. Pharm. Chim.*, 1902, [vi], 15, 573—577).—When an animal is injected with the blood serum of an animal of a different species, the serum of the injected specimen acquires, after a period of a few days, the property of precipitating fresh serum obtained from the source of the injection. This property is not strictly specific: thus serum obtained from a rabbit originally injected with human blood serum, precipitates the latter copiously, and, in a less degree, fresh serum obtained from the dog, sheep, pig, guinea-pig, &c. All albuminous liquids produced in metabolic processes are sensitive to serum cultivated in this manner, and, conversely, such serum can be prepared by the injection of other metabolic liquids, such as urine, &c. The author discusses the experimental results which have led to these conclusions, and makes suggestions for the application of these results to the characterisation of specimens of blood and the sources of the pathological proteids of urine.  
T. A. H.

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## Chemistry of Vegetable Physiology and Agriculture.

**Preparation of Permanent Yeast with Acetone.** By ROBERT ALBERT, EDUARD BUCHNER, and RUDOLF RAPP (*Ber.*, 1902, 35, 2376—2382).—The activity of yeast can be preserved by drying at a low temperature and then sterilising by heat (Buchner, *Abstr.*, 1897, ii, 380, and 1901, i, 179) or by killing with alcohol and ether (Albert, *Abstr.*, 1901, i, 180). Better results are obtained when the yeast is killed with acetone. The product is a white, dusty powder, containing 5.5—5.6 per cent. of water, and the yield of dried yeast is 30 to 32 per cent. In 72 hours, the dried yeast will decompose about its own weight of sucrose, and liberate about half its weight of alcohol. The activity of the yeast decreased in two cases by only 10 and 19 per cent. respectively after keeping for six months, and only one sample out of eighteen was found to be imperfectly sterilised. The acetone-yeast is more active than that dried by alcohol and ether, probably because the destructive action of the alcohol is eliminated; the fermentation also proceeds much more rapidly, the acetone-yeast liberating as much carbon dioxide in an hour as the alcohol-ether yeast in 3 hours.  
T. M. L.

**Effect of Nitrogen on Nitrates, and of Humous Substances on the Inoculation of Leguminous Plants.** By FRIEDRICH NOBBE and L. RICHTER (*Landw. Versuchs-Stat.*, 1902, 56, 441—448).—Pot experiments are described in which oats and soy beans, both separately and mixed, were grown in humous soil and a mixture of the soil with sand. In each case, one set of pots was inoculated, the other not; and in the case of the mixed soil there were additional pots which received potassium nitrate (5 and 10 grams respectively). The inoculation was effected by means of an extract of soy bean soil from Japan.

It was found that the effect of inoculation was diminished both by the nitrogenous matter of the soil and by the nitrate added. The activity of the nodule bacteria was increased when oats were grown with beans, owing to the oats taking the nitrates from the soil.

The yield of oats was greater when the oats were grown with beans than when grown alone.  
N. H. J. M.

**Amino-acids as Food Material for Lower Forms of Plant Life.** By OSKAR EMMERLING (*Ber.*, 1902, 35, 2289—2290).—Only certain amino-acids can act as food material for moulds, and even closely allied acids behave in very different manner. Of  $\alpha$ - and  $\beta$ -amino-acids, the former only can act as food material and these only for certain moulds.  $\gamma$ -Aminobutyric acid is an excellent food for all the moulds investigated;  $\alpha$ -aminobutyric acid, *i*-leucine, and tyrosine are of but little value as food supplies. Of the aromatic compounds, 2-pyrrolidinecarboxylic acid is one of the most nutritious foods, and so also to a certain extent is phenylalanine.

$\alpha$ -Amino- $\beta$ -hydroxypropionic acid is an admirable food, but  $\beta$ -amino- $\alpha$ -hydroxypropionic acid is absolutely useless.

The experiments were made with *Penicillium glaucum*, *Aspergillus niger*, *A. clavatus*, *A. oryzae* and *Mucor mucedo*. The results are not always the same with different moulds. J. J. S.

**Function of Peroxides in Cell-life.** By A. BACH and ROBERT CHODAT (*Ber.*, 1902, 35, 2466—2470. Compare this vol., ii, 344).—The oxydases of the plant cell have the power of forming peroxides in the presence of free oxygen, and these can be detected by the liberation of iodine from hydriodic acid. The juice of *Lathræa squamaria* contains an oxydase, which turns tincture of guaiacum blue, and in the presence of oxygen this juice yields, with barium hydroxide, a precipitate which liberates iodine from hydriodic acid, but does not react with titanous and sulphuric acids. This substance, therefore, has the properties of an acylated hydroperoxide. When the juice is kept until the guaiacum reaction disappears, the peroxide reaction also disappears. Liberation of iodine is also brought about by the freshly-cut stems of a large number of plants, and the peroxide may be detected by the same reaction in the living cells of the potato.

A. H.

**Has Hydrogen Peroxide a Function in Cell-life?** By OSCAR LOEW (*Ber.*, 1902, 35, 2487—2488).—The facts adduced by Chodat and Bach (this vol., ii, 344) do not prove the presence of hydrogen peroxide in the cells of the moulds growing in solutions containing this substance. Since these moulds are very rich in catalase their comparative immunity towards hydrogen peroxide may be due to the rapidity with which the cell is able to decompose this substance.

A. H.

**Decomposition of Carbohydrates in Germinating Dates.** By J. GRÜSS (*Chem. Centr.*, 1902, i, 942; from *Ber. deut. bot. Ges.*, 20, 36—44).—Whilst  $\alpha$ -mannan from date seeds yields mannose in presence of malt or yeast diastase, Reiss failed to detect mannose in germinating dates.

By keeping endosperms from date plants two months old in water with thymol as antiseptic, a solution was obtained which contained mannose, as well as galactose, sucrose, and invert sugar. The amount of reducing sugar is less than 1 per cent. of the weight of the endosperm. The sucrose was no doubt present in the embryo before germination. N. H. J. M.

**Transformations of Proteids during Germination.** By GUSTAVE ANDRÉ (*Compt. rend.*, 1902, 134, 995—998).—The total nitrogen and the nitrogen as proteids, legumin, and soluble amides, was determined in haricot seeds and in seedlings at five different periods from June 1 to June 13.

The results showed that the production of new proteids commenced when the weight of the dry matter of the seedlings reached that of the original seeds. At the same time, the total nitrogen which had remained stationary began to increase.

The legumin diminished rapidly during germination, but did not disappear completely. When, however, the seeds were germinated in darkness, the seedlings (a month old) were found to have lost the whole of the legumin and albumin, whilst the soluble nitrogen amounted to 83.5 per cent. of the total.

N. H. J. M.

**Transpiration of Apples.** By RICHARD OTTO (*Landw. Versuchs-Stat.*, 1902, 56, 427—439. Compare Abstr., 1901, ii, 678).—The results of experiments in which apples were kept under a bell jar showed that there was a slight loss of water in nearly every case. The whole of the starch disappeared in 23 days, whilst the invert sugar increased. The sp. gr. of the must was increased by transpiration, especially in the case of unripe fruit. The amount of malic acid diminished, whilst there was an increase in the amount of extract. A second series of experiments is described, in which the apples were kept under the usual conditions.

The conclusion is drawn that transpiration is advantageous to the production of cider in the case of unripe apples, especially when they contain much starch, provided that the process is not of too long duration (more than 3—4 weeks).

N. H. J. M.

**The Boric Acid Controversy.** By EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1902, 26, 465).—Attention is called to the natural occurrence of traces of boric acid in lemons, oranges, and other fruits grown in southern climes.

L. DE K.

**Acids of Bignonia Catalpa.** By ARNALDO PIUTTI and E. COMAN-  
DUCCI (*Bull. Soc. Chim.*, 1902, [iii], 27, 615—620).—From the unripe fruits of *Bignonia catalpa*, the authors have obtained *p*-hydroxybenzoic acid (Sardo's catalpic acid, Abstr., 1885, 272) and a compound of *p*-hydroxybenzoic and protocatechuic acids,  $C_7H_6O_3 \cdot C_7H_6O_4 \cdot 2H_2O$ . They incline to the belief that these acids exist in the fruit in the form of glucosides, but this point is being further investigated.

A. F.

**Prussic Acid in the Opening Buds of Prunus.** By E. VER-  
SCHAFFELT (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 5, 31—41).—The hydrocyanic acid present in the buds of *Prunus Laurocerasus* and *P. Padus* increases in amount in the fresh shoots, whether grown in the light or in the dark. The hydrocyanic acid is present as a glucoside similar to amygdalin, and is not drawn from the internodes of the previous year's growth.

G. Y.

**Mechanism of the Chemical Changes in Plants Subjected to the Influence of Sodium Nitrate.** By EUGÈNE CHARABOT and ALEXANDRE HÉBERT (*Compt. rend.*, 1902, 143, 1228—1230).—Six rows of peppermint plants about 4 metres long were watered on May 23rd with a solution of 500 grams of sodium nitrate in 20 litres of water and the proportions of water, organic matter, esters, and essential oils in the plants were determined from time to time. The results show that when the plant reaches a suitable stage of development the relative proportion of water diminishes and the proportion of organic



matter increases more markedly under the influence of sodium nitrate than under normal conditions. Sodium nitrate also causes the production of an essential oil constantly richer in esters and poorer in menthol and menthone than that formed under normal conditions. The effect of sodium nitrate is therefore similar to that of sodium chloride, although the mechanism of the influence is probably not the same, since sodium nitrate increases the chlorophyllien function whilst sodium chloride reduces it. C. H. B.

**Number and Depth of Roots of Different Plants with Various Manures.** By CONRAD VON SEELHORST (*J. Landw.*, 1902, 50, 91—104. Compare Abstr., 1899, ii, 508).—The results obtained with a variety of plants showed that manuring increased, not only the development of the roots, but also their depth in the soil. The soil on which the experiments were made was very uniform, and it is suggested that divergent results might be obtained when the subsoil differs to any extent from the surface soil. The results are of practical importance as they indicate that one effect of manuring, at any rate on suitable soils, is to increase the power of crops to resist the effects of drought by increasing the depth of the roots. N. H. J. M.

**Chicory and the Production of Leaves.** By EM. CARPIAUX (*Bied. Centr.*, 1902, 31, 403—406; from *Bul. Inst. Gembloux*, 1901, No. 70, 17).—When chicory roots were allowed to produce new growth much of the inulin (20 per cent.) was utilised. Of the ash constituents, the roots lost much of the potassium but very little of the phosphoric acid originally present. There was also a considerable reduction (about 15 per cent.) in the total nitrogen of the roots. The nitrogenous substances, both proteids and non-proteids, undergo, however, no essential change, but merely migrate to the newly-formed growth. N. H. J. M.

**Manurial Experiments with Potassium and Phosphoric Acid on Barley.** By THEODOR REMY and O. NEUMANN (*Bied. Centr.*, 1902, 31, 374—379; from *Bl. Gersten-, Hopfen-, u. Kartoffelbau*, 1901, 227, 261, 305, and 337).—Twenty-nine field experiments were made in different parts of Germany in which barley was grown without manure, with 12·5 lb. of potash (as 40 per cent. potassium salts), with 10 lb. of phosphoric acid (as superphosphate), and with the same amounts of potassium salts and superphosphate together per half morgen. On the whole, the two manures had almost the same effect on the production of grain, whilst potassium had the greater effect on straw production. The results varied according to the nature of the soil. The percentage number of cases in which the manures were decidedly effective on light and heavy soils respectively are as follows :

	Potassium salts.	Superphosphate.	Both manures.
Light soils.....	42·9	64·3	85·7
Heavy soils .....	83·3	83·3	100·0

Vegetation experiments were made with the same soils in pots.

Potassium was applied as chloride and phosphoric acid as monocalcium salt, and all the pots received nitrogen (as ammonium nitrate) and calcium carbonate. The amounts of proteids in the grain varied only slightly. Phosphoric acid increased the yield without increasing the weight of the grains. Potassium, on the other hand, increased both the yield and the weight of the grains, the number of grains being unaltered.

N. H. J. M.

**Manurial Experiments with Barley.** By RUDOLF ULRICH (*Bied. Centr.*, 1902, 31, 380—381; from *Fühling's Landw. Zeit.*, 1900, 533).—As regards the effect of manuring on the quality of barley, it was found that the application of manures increased the percentage of water, and, especially in the case of potassium manures, the amount of starch in the air-dried grain, and that nitrogenous manures increased the percentage of proteids, which was diminished by potassium and phosphatic manures when applied in large amounts. The percentage of starch increases almost equally with the dry matter.

Peruvian guano containing N, 7;  $K_2O$ , 4; and  $P_2O_5$ , 10.5 per cent. is recommended for barley.

N. H. J. M.

**Rye and Wheat.** By F. BARNSTEIN (*Landw. Versuchs-Stat.*, 1902, 56, 369—418).—The paper contains analyses of rye and wheat grain, bran, and meal by different investigators, as well as some new analyses; the botanical characters of the plants and the feeding values of bran and meal are also discussed in detail.

N. H. J. M.

**Digestion of Maize by Fowls.** By SIMEON PARASCHTSCHUK (*J. Landw.*, 1902, 50, 15—32).—The results of experiments with fowls indicate that they digest the constituents of maize to about the same extent as larger animals; the results resemble those furnished by pigs rather than those obtained with horses and cattle. Previous investigators obtained much lower results as regards crude fibre.

N. H. J. M.

**Relation of the Chemical Composition and Anatomical Character to the Value of Potato Tubers.** By FR. WATERSTRADT and M. WILLNER (*Bied. Centr.*, 1902, 31, 329—331; from *Bl. Gersten-, Hopfen-, u. Kartoffelbau*, 1901, 293).—The outer layer of fresh potatoes contains considerably more starch, crude fibre, and, generally, proteid, but less non-proteid nitrogen, and usually less total nitrogen than the marc. The amounts of proteid nitrogen and starch in the dry matter of the outer layer do not differ much from those in the dry matter of the marc, but as a rule the latter contains rather more proteids.

In the case of varieties of potatoes which give large yields, the tubers contain relatively more marc tissues than varieties which give small yields. There seems to be no relation between the feeding value of potatoes and the amounts of dry matter, starch, and nitrogen, &c., which they contain, but in the better varieties it is found that the relation between starch and total nitrogen is a narrow one.

N. H. J. M.

**Relation between the Amounts of Phosphoric Acid and Ammonia in Plants, especially in Sugar-beets.** By HENRI PELLET (*Zeit. Ver. deut. Zuckerind.*, 1902, 555, 390—393).—It was shown by Champion and Pellet (*Abstr.*, 1876, 420, and 1880, 569) that plants always contain ammoniacal nitrogen, and that the quantities of ammonia and phosphoric acid present are such as are required for the formation of ammonio-magnesium phosphate. The author now gives the results of an examination of Egyptian beets grown in soil formed by the gradual accumulation of Nile mud and containing only traces of either ammonia or nitric acid. In this case also, however, the above relation between the quantities of ammonia and phosphoric acid is found to hold. T. H. P.

**Action of Nitrogen in Absence of other Nutritive Substances.** By H. WILFARTH (*Bied. Centr.*, 1902, 31, 430—431; from *Bl. Zucker-rübenbau*, 1901, 15).—Sugar-beets grown without potassium and with little nitrogen contained 11.03 per cent. of sugar. With large amounts of nitrogen, but without potassium, the roots contained 0.0062 per cent. of sugar. Potatoes, similarly manured, contained 14.6 and 9.76 per cent. of starch respectively. Exclusive nitrogenous manuring has therefore the reverse of the desired effect. N. H. J. M.

**Alterations in the Composition of the Beet during Ripening.** By KARL ANDRLÍK, VL. STANĚK, and K. URBAN (*Zeit. Zuckerind. Böhm.*, 1902, 26, 343—363).—The authors have made exhaustive analyses of the leaves, leaf-stems, and roots of beets pulled at different times during the harvest. An account is given of the methods employed and results obtained, and also of those of previous workers in this direction.

The analytical numbers show that the value of the leaves and leaf-stalks as manure diminishes during the maturation of the plant, but that their food-value remains practically unaltered. The quality of the roots is improved very considerably owing to a diminution in the amount of alkalis, nitrogen, and reducing matters. T. H. P.

**Cultivation of Mangels on the Experimental Fields at Grignon in 1900 and 1901.** By PIERRE P. DEHÉRAIN and C. DUPONT (*Compt. rend.*, 1902, 134, 953—958).—Sugar mangels gave decidedly better results than the older kinds. The red variety is most suitable for dry soils and the white variety for wet soils.

N. H. J. M.

**Production of Milk and Butter. Variations in the Composition of Butter.** By L. MALPEAUX and J. DELATTRE (*Ann. Agron.*, 1902, 28, 209—223. Compare this vol., ii, 168).—Beet pulp does not affect the taste of butter as sometimes stated; it may cause a reduction in the amount of volatile acids, and the same effect is produced by brewer's grains and green fodder. Horse beans increased the volatile acids. Oleaginous foods greatly alter the composition of butter by causing a reduction in the percentage of volatile fatty acids.

The effects of race, individuality, period of gestation, and season are also discussed.  
N. H. J. M.

**The Influence of Feeding on the Composition of the Fat of Milk.** By B. SJOLLEMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 6, 746—756).—In some parts of the Netherlands at certain seasons the butter obtained has a high refraction number and a low Reichert-Meissl-Wollny number, which depends on the small amount of volatile fatty acid. Such butter is suspected of adulteration and its sale has been prohibited in some countries. The peculiarity is largely dependent on feeding. Feeding on beet foliage raises the R.M.W. number, and experiments with molasses indicate that it is mainly the sugar contained in the beet-leaves which acts favourably by increasing the amount of lower fatty acids.  
W. D. H.

**Chemical Changes in Peat Soil after Several Years' Cultivation and Manuring.** By HJALMAR VON FEILITZEN (*Bied. Centr.*, 1902, 31, 362—365; from *Svenska Mosskulturfor. Tidskr.*, 1901, 319—329).—The soil of the experimental field at Flahult consists mainly of very slightly decomposed peat, about 3 metres deep. Some of the plots had an application of sand (500 cubic metres per hectare); it was found after 8 years that practically the whole of the sand remained near the surface.

Analyses of the soil made in 1892, 1894, and 1900 showed that the nitrogen, potassium, and phosphoric acid increased in the course of six years. The surface soil of the plots to which sand had been added gained less phosphorus, but more potassium, than those which did not have an application of sand. The percentage of nitrogen showed a marked increase, but for cereals and root crops it is necessary to apply nitrogenous manures.

In addition to the peat soil, the Flahult experiments include plots on humified peat containing 2.89 per cent. of nitrogen. Some plots remained without sand, others had an application of sand which was mixed with the soil, whilst a third series received a layer of sand. The surface soil became considerably richer in phosphoric acid during the experimental period, and there was also a gain of potassium, but considerable amounts of potassium and calcium descended to the subsoil.

N. H. J. M.

**Manurial Experiments on Peat Land.** By HJALMAR VON FEILITZEN (*J. Landw.*, 1902, 50, 77—90. Compare Abstr., 1896, ii, 269).—A *résumé* of results of some of the experiments conducted at Jönköping and Flahult during the last 13 years.

The peaty soil contains very little potash. A certain amount of potash is frequently supplied in sand or loam applied to the land, but, as a rule, manuring with potassium is of great importance. The potassium of peat soil is comparatively readily soluble and a good deal may be lost in drainage; a certain amount is, however, retained by the soil and this amount tends to increase.

The Swedish peat soils are very poor in phosphoric acid with the few exceptions of those which contain vivianite, and even these

require applications of phosphoric acid from time to time. Basic slag, superphosphate, and Wiborgh phosphate are about equally suitable manures for peat soil; bone meal, Algerian, Somme, and Belgian phosphates are less suitable, whilst apatite, Lahn phosphorite and Red-onda phosphate are too insoluble in undecomposed peat land. The soil retains phosphoric acid with great tenacity, and the drainage contains only traces of phosphoric acid.

Whilst one variety of peat soil is very rich in nitrogen, the other ("Hochmoor") contains very little. Of the different manures (sodium nitrate, ammonium sulphate, and fish guano), sodium nitrate is the most suitable for peat land. The chief value of dung when applied to peat is in connection with the microbes thus introduced, as they are of importance in the decomposition of the insoluble nitrogenous matter.

N. H. J. M.

**Manurial Action of Bone Meal Phosphoric Acid.** By OSCAR KELLNER and O. BÖTTCHER (*Bied. Centr.*, 1902, 31, 305—307; from *Deut. landw. Presse*, 1901, Nos. 23 and 24. Compare Abstr., 1901, ii, 275).—The unfavourable results obtained with bone meal by Wagner and Maercker are attributed to the simultaneous application of calcium carbonate and to the experiments having been made on soil rich in calcium.

The slower action of bone meal as compared with basic slag and superphosphate is shown by applying the three manures in the spring to a quick-growing plant such as white mustard; in this case, the bone meal gave very inferior results as compared with the other two manures. Addition of 15 grams of calcium carbonate to the 3.5 kilos. of soil reduced the yield in each case, but to the largest extent with bone meal. A greater amount of carbonate (30 grams) had very little or no further effect in reducing the yield where basic slag and superphosphate were employed, but in the case of bone meal reduced the yield by about 50 per cent.

The conclusion is drawn that phosphoric acid should not be applied to soils when limed, unless the soil has already received plenty of phosphoric acid.

N. H. J. M.

**[Manurial] Action of Nitrogen as Nitrates and as Ammonia.** By MAX GERLACH (*Bied. Centr.*, 1902, 31, 371—372; from *Jahresber. Landw. Versuchs-Stat. Posen*, 1900—1901, 11).—The effect of nitrogen in the form of sodium nitrate and as ammonium salts is almost the same when the soil contains sufficient amounts of sodium, potassium, and calcium. But sodium nitrate gives decidedly better results than ammonium salts when the soil is deficient in these substances.

N. H. J. M.

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## Analytical Chemistry.

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**New Form of Abich's Mortar.** By W. I. IWANOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 397).—The author proposes to modify the well-known steel mortar used for powdering minerals by cutting the cylindrical portion, in which the pestle fits, longitudinally into two halves, these being held together by a ring which screws on to the base. Such an arrangement, views of which are given, allows of the mortar being readily taken to pieces. T. H. P.

**The Literature of Volumetric Solutions and the Substances employed for Standardising them.** By LUDWIG VANINO and E. SEITTER (*Zeit. anal. Chem.*, 1902, 41, 141—218).—A compendium of the processes and materials employed for preparing standard solutions, with references to the original papers. M. J. S.

**Inapplicability of Winkler's Method of Fractional Combustion of the Hydrogen to the Examination of Natural Gas.** By K. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 393—395).—In determining hydrogen when mixed with methane, Winkler recommends the combustion of the hydrogen by means of slightly palladinised asbestos. This method cannot, however, be employed for natural gases, since these contain constituents, such, for instance, as *isopentane*, which would undergo oxidation at the same time as the hydrogen. T. H. P.

**Estimation of Perchlorate in Saltpetre.** By AUGUSTE DUPRÉ (*J. Soc. Chem. Ind.*, 1902, 21, 825—826).—Twenty grams of the sample are introduced into a covered 70 c.c. nickel crucible and the perchlorate is reduced to chloride by heating for an hour in a Gilbert's furnace at 545°. The mass is then dissolved in water and the solution made up to 200 c.c. After estimating the chlorine in 25 c.c. by Mohr's method, 100 c.c. are precipitated with a small excess of standard silver solution (1 c.c. = 0.001 chlorine), 4 c.c. of strong nitric acid are added, and after boiling and subsequent cooling the liquid is filtered and the excess of silver estimated by Volhard's thiocyanate method.

Allowance must, of course, be made for any chloride existing as such; this is estimated in 10 grams of the original sample as directed. L. DE K.

**Detection of Fluorides in Butter.** By OTTO HEHNER and CHARLES W. HEHNER (*Analyst*, 1902, 27, 173—179).—Fifty grams of the butter are melted in a beaker after rendering slightly alkaline. The aqueous portion is drawn off, a little calcium chloride is added, the liquid is heated to boiling, and a small excess of sodium carbonate added to precipitate the calcium compounds. The precipitate, consisting of calcium borate (if borates be present in

the butter), fluoride, carbonate, phosphate, and probably sulphate, is filtered off, ignited, and treated with hot dilute acetic acid to dissolve out the carbonate, borate, and phosphate. The residue is again collected on a filter, washed, and ignited in a platinum crucible. When cold, a drop of concentrated sulphuric acid is added and the crucible covered with a waxed glass plate on which scratches have been made with a pin. The crucible and its contents are then gently heated on a sand-bath for 2 hours. Should fluorides be present, the glass is etched. It was found that 1 mg. of calcium fluoride gave a distinct etching on the glass. W. P. S.

**The "Natromètre."** By DÉMICHEL (*Ann. Chim. anal.*, 1902, 7, 204—209).—A mathematical criticism of Pésier's old and new "natromètre" unsuitable for useful abstraction. L. DE K.

**Test for Nitrogen in Pyrrole Compounds by Lassaigue's Method.** By EDUARD A. KEHRER (*Ber.*, 1902, 35, 2523—2525).—The usual procedure is altered, so that the sodium (or potassium) is heated first in a constriction of the test-tube, and then the substance, which has been placed in the wider portion. The vapours of the substance thus pass over the molten metal with a more certain formation of cyanide. R. H. P.

**Arsenic in Glycerol.** By J. BOUGAULT (*J. Pharm. Chim.*, 1902, [vi], 15, 527—529).—The method employed by Engel and Bernard (*Abstr.*, 1896, ii, 448) is recommended for the detection of arsenic in glycerol. 0.004 gram per litre can be readily detected by this process. T. A. H.

**Separation of Arsenic, Tin, and Antimony.** By WILLIAM R. LANG, C. M. CARSON, and J. C. MACKINTOSH (*J. Soc. Chem. Ind.*, 1902, 21, 748).—The solution containing the hydrochloric acid solution of the three metals is, if necessary, first reduced by means of sulphur dioxide, and the metals are then precipitated as sulphides. The washed precipitate is evaporated to dryness with 15 c.c. of strong nitric acid, the residue treated with 100 c.c. of warm water, and the arsenic acid in the filtrate precipitated, as usual, with magnesia mixture, and finally weighed as pyroarsenate. The antimony is then separated from the tin oxide by digesting for an hour with solution of tartaric acid, and the undissolved tin oxide ignited and weighed. The antimony is precipitated by adding a little hydrochloric acid and passing hydrogen sulphide, the sulphide is then converted into oxide by nitric acid, and, after ignition, weighed as the tetroxide.

Experiments made to quantitatively separate the sulphides of tin and antimony from arsenic trisulphide by means of strong hydrochloric acid were unsuccessful, as a varying amount of arsenic trisulphide also dissolves. L. DE K.

**Rapid Estimation of Boric Acid in Butter.** By H. DROOP RICHMOND and JOHN B. P. HARRISON (*Analyst*, 1902, 27, 179—181).—Twenty-five grams of the butter are weighed out into a beaker, and

25 c.c. of a solution containing 6 grams of milk sugar and 4 c.c. *N* sulphuric acid in 100 c.c. are added. The beaker is placed in the water-oven until the fat has just melted, and the contents are stirred well. After allowing the aqueous portion to settle for a few minutes, 20 c.c. are drawn off, a little phenolphthalein added, brought to the boiling point, and titrated with *N*/2 soda until a faint pink colour just appears. Twelve c.c. of neutral glycerol are now added, and the titration continued until a pink colour appears. The difference between the two titrations multiplied by 0.0368 gives the amount of boric acid in 20 c.c., and this, multiplied by  $\frac{100 + \text{percentage of water in the butter}}{20}$

will give the percentage of boric acid. The estimation is not affected by the phosphoric acid, butyric acid, or milk sugar present in the butter.

W. P. S.

**New Process for the Volumetric Evaluation of Red Lead.** By E. SZTERKHERS (*Ann. Chim. anal.*, 1902, 7, 214—217).—A solution is made containing exactly 10 grams of recrystallised sodium nitrite per litre. By means of this solution, a solution of potassium permanganate containing approximately 8 grams of this salt per litre is standardised as follows: 50 c.c. of dilute sulphuric acid (1 : 4) and 300 c.c. of water are heated to 40°, 50 c.c. of the permanganate are introduced, and the nitrite is then added with constant agitation until the liquid is decolorised.

Five grams of the sample of red lead are heated with 100 c.c. of boiling water and 5—7 c.c. of pure nitric acid for 15 minutes on the water-bath. After cooling to 50°, the nitrite is added drop by drop until the dioxide has completely dissolved, and after noting the amount used, the excess of nitrite is titrated with permanganate. The number of c.c. of nitrite solution decomposed by the red lead multiplied by 0.693 equals the percentage of lead dioxide in the sample. Absolutely pure red lead contains 34.8 per cent. of lead dioxide.

L. DE K.

**Thallium. I. Estimation of Thallium in the Thallous State.** By VICTOR THOMAS (*Bull. Soc. Chim.*, 1902, [iii], 27, 470—471).—In estimating thallium, the author oxidises the thallous salt to thallic salt by means of hydrobromauric acid, the latter being reduced with deposition of metallic gold, according to the equation  $3\text{TiCl} + 2\text{AuBr}_3 = 3\text{TiClBr}_2 + 2\text{Au}$ .

The hydrobromauric acid is easily obtained by dissolving gold in hydrobromic acid containing bromine and evaporating on the water-bath, when it is deposited in long, dark coloured needles.

A. F.

**Volumetric Estimation of Copper by Potassium Iodide.** By FRANZ M. LITERSCHIED (*Zeit. anal. Chem.*, 1902, 41, 219—227).—Besides the method of Mohr (*Lehrbuch*) and Vitali (*Abstr.*, 1895, ii, 140), a process may be based on the measurement of the amount of potassium iodide consumed in precipitating the copper as cuprous iodide in presence of sulphurous acid. The neutral or feebly acid (sulphuric, nitric, or acetic acid, compare Low, *Eng. and Min. Journ.*, 1895, 124) cupric solution is mixed with sulphurous acid and a small



excess of  $N/10$  potassium iodide. After reposing for an hour for the precipitate to aggregate, the whole is made up to a known volume (200—500 c.c. for 0.1 gram of copper), and to an aliquot part of the clear solution an excess of  $N/10$  silver nitrate is added. The excess of silver is then titrated by Volhard's thiocyanate method. The presence of nickel and zinc requires no modification of the process. Silver can be estimated by converting the metals into sulphates and titrating the silver by potassium iodide in presence of a trace of a nitrite with starch as indicator. The entire mixture is then treated as above for the estimation of the copper. If bismuth is also present it must be separated as oxychloride, or, in the absence of silver, the bismuth may be removed as basic carbonate and the ammoniacal filtrate at once acidified with acetic acid and used for the estimation of copper. Lead must be separated as sulphate, tin as metastannic acid, before employing the process for titrating the copper. M. J. S.

**Volumetric Estimation of Copper.** By SAMUEL W. PARR (*J. Amer. Chem. Soc.*, 1902, 24, 580—581).—A slight modification of the method recently communicated (Abstr., 1900, ii, 762).

The washed cuprous thiocyanate, together with the asbestos, is returned to the beaker. Ten c.c. of a 10 per cent. solution of potassium hydroxide and then 10 c.c. of ammonia of sp. gr. 0.96 are added, and the mixture is without delay titrated with standard permanganate, until on warming to 45—55° the green colour remains. About one-fourth of the quantity of permanganate already used is added, and after cooling for five minutes 25 c.c. of dilute sulphuric acid (1:2) are added and the titration continued to the end. The reaction is sharp and the results are concordant. L DE K.

**Electrolytic Estimation of Mercury.** By EMIL BINDSCHIEDLER (*Zeit. Elektrochem.*, 1902, 8, 329—332).—The estimations, made by electrolytic deposition of the mercury on a matt-surfaced platinum dish, from solution in sulphuric acid or potassium cyanide, were always too low. The reason was found in the evaporation of the deposited mercury, which is readily avoided by keeping the temperature as low as possible and taking care that the deposit of mercury is always covered by the electrolyte. The results are then very accurate. T. E.

**Stukowenkow's Method for the Estimation of Mercury in Urine.** By BRUNO BARDACH (*Zeit. anal. Chem.*, 1902, 41, 232—235).—An attempt to obtain quantitative results by the method described in Abstr., 1901, ii, 579, by comparing the rings of mercuric iodide with standards, showed that under the conditions laid down by Malkes (*Chem. Zeit.*, 1900, 24, 816) no such results are obtainable. Although 5 c.c. of egg-albumin precipitates traces of mercury completely from 500 c.c. of urine, the precipitation becomes incomplete when the mercury amounts to 3.5 mg. Further, the precipitation by a copper spiral is very imperfect unless the quantity of copper gauze used is so much increased that the subsequent expulsion of the mercury, and its

collection as iodide in a definite ring, are seriously impeded. The method can therefore only be employed as a rough qualitative one.

M. J. S.

**Use of Persulphates in Analysis.** By HENRY D. DAKIN (*J. Soc. Chem. Ind.*, 1902, 21, 848—849).—*Estimation of Manganese.*—Manganese is completely precipitated by adding to the solution, heated at 50°, a solution of ammonium persulphate followed by a moderate excess of ammonia. The precipitate does not lend itself to volumetric estimation owing to the variable composition of the oxide formed, but the gravimetric determination as manganous sulphate is satisfactory.

*Oxidation of Chromium Salts.*—Chromic salts are completely converted into chromates by boiling with large excess of potassium or sodium hydroxide and adding potassium persulphate. Attempts to substitute the ammonium compounds for the fixed alkalis ended unsatisfactorily.

*Estimation of Nitrogen.*—The author believes that potassium persulphate will be a great service in Kjeldahl's process. After heating for a while with the usual mixture of sulphuric acid and potassium sulphate, the acid is allowed to cool below 100° and a few grams of the persulphate are added; if not yet fully oxidised, the liquid should be again heated, and after cooling again treated with persulphate. It is probable that ammonium persulphate may be useful for the destruction of organic matter in toxicological investigations. L. DE K.

**Qualitative Test for Cobalt.** By J. L. DANZIGER (*J. Amer. Chem. Soc.*, 1902, 24, 578—580).—About 5 c.c. of the solution acidified with hydrochloric acid are mixed in a test-tube with some solid ammonium thioacetate, a few drops of solution of stannous chloride are added, and the mixture is shaken with 5 c.c. of amyl alcohol. In the presence of cobalt, the upper layer will show a more or less decided blue colour. Instead of amyl alcohol, a mixture of acetone and ether, or of alcohol and ether, may be used, but amyl alcohol is most efficient.

The reaction is due to the formation of a double compound of ammonium and cobaltous thioacetate. One part of cobalt may thus be detected in 500,000 parts of liquid. The addition of stannous chloride serves to reduce any ferric iron. L. DE K.

**Volumetric Estimation of Molybdenum in Molybdenum Steel and Ferro-Molybdenum.** By JAMES BRAKES (*J. Soc. Chem. Ind.*, 1902, 21, 832).—A modification of Kopp's method (this vol., ii, 430). Five grams of the sample are dissolved in a beaker in a mixture of 20 c.c. of nitric acid and 20 c.c. of hydrochloric acid and evaporated to dryness; the mass is redissolved in 10 c.c. of hydrochloric acid, 20 c.c. of dilute sulphuric acid (1 : 1) are added, and the solution is evaporated until fumes of sulphuric acid appear. When cold, 400 c.c. of water are added and the liquid is heated until solution is complete. The solution is now transferred to a litre flask, 100 c.c. of ammonia of sp. gr. 0.90 are added, and after standing in cold water for an hour the contents are made up with water to the mark. Five hundred c.c.

of the filtrate are mixed with 40 c.c. of sulphuric acid of sp. gr. 1.60, passed through the reductor, and titrated with permanganate. After deducting the amount indicated by a blank experiment, the value of the permanganate in iron is multiplied by 0.605. Tungsten must be removed before the evaporation with sulphuric acid; chromium exercises no influence on the titration, even when as much as 8 per cent. is present.

L. DE K.

**Technical Estimation of Tin in Solutions of Pink Salt.** By OSKAR GEISEL (*Chem. Zeit.*, 1902, 26, 553—554).—The solution, which should not contain any excess of hydrochloric acid, is titrated with *N*/10 sodium hydroxide, using malachite-green as indicator, until the liquid turns a pure blue, which does not get darker on adding more sodium hydroxide.

It is essential that the liquid should only contain from 0.075—0.100 gram of tin oxide in 10 c.c., to which a sufficiency of a 1 per cent. solution of malachite-green is added. Seven mols. of sodium hydroxide represent 2 mols. of stannic chloride. The test analyses seem promising.

L. DE K.

**Aromatic Bases as Precipitants for Rare Earth Metals.** By ALICE MACMICHAEL JEFFERSON (*J. Amer. Chem. Soc.*, 1902, 24, 540—562).—Zirconium nitrate is quantitatively precipitated by aniline, *o*-toluidine, xylidine, dimethylamine, diethylamine, benzylamine, pyridine, piperidine, and quinoline, but phenylhydrazine gives no precipitate. Thorium nitrate is also precipitated; benzylamine and diphenylamine were not tried, and phenylhydrazine gives a precipitate soluble in excess. Cerium nitrate is quantitatively precipitated except by xylidine, dimethylamine, and quinoline, whilst phenylhydrazine and diphenylamine give no precipitate at all.

Lanthanum chloride or its double ammonium nitrate compound is quantitatively precipitated by benzylamine and piperidine, but only partially so by pyridine and phenylhydrazine, whilst the other bases give no precipitate; diphenylamine was not tried. The same remarks practically apply to praseodymium and neodymium.

**Separations.**—Thorium may be quantitatively separated from neodymium by precipitating the nearly neutralised solution with quinoline; in the same way, zirconium may be separated from neodymium. Thorium may be separated from lanthanum by aniline. Zirconium may also be separated from lanthanum in the same manner. Thorium may also be separated quantitatively from lanthanum by precipitation with quinoline. Cerium may be separated from praseodymium by means of *o*-toluidine. Thorium is separated from praseodymium by means of aniline. Zirconium may be separated from lanthanum and also from praseodymium by means of xylidine. (For minute details to be observed in the separations, the original article should be consulted.)

L. DE K.

**New Apparatus in Water Analysis.** By GEORGE E. THOMAS and CLARENCE A. HALL (*J. Amer. Chem. Soc.*, 1902, 24, 535—539).—A description of a battery of six stills used in the determination of

ammonia in water by the Wanklyn method; of an apparatus for collecting samples of water for the purpose of estimating the dissolved oxygen or carbon dioxide, and of an arrangement for collecting suspended matter on asbestos. Full illustrations are given. L. DE K.

**Estimation of Ammonia in Waters.** By OSKAR EMMERLING (*Ber.*, 1902, 35, 2291).—Proteids interfere with the usual estimation of ammonia by Nessler's reagent. It is therefore necessary that waters containing proteids should be boiled with magnesia or lead oxide and the ammonia estimated in the distillate. J. J. S.

**Estimation of Nitrates in Water by the Indigo-Carmin Method.** By SAMUEL R. TROTMAN and HAROLD PETERS (*J. Soc. Chem. Ind.*, 1902, 21, 694—695).—Five to 20 c.c. of the sample of water are mixed with 25 c.c. of (Löwenthal's) indigo-carmin solution, and to the liquid is added an equal bulk of sulphuric acid; the whole is then heated on the sand-bath for 15 minutes. At the same time, a blank determination is made with distilled water and indigo-carmin. Both solutions are then titrated with standard permanganate, and the difference between the two titrations represents the nitrogen. The permanganate is standardised by means of a solution of potassium nitrate containing 0.0001 gram of nitrogen per c.c. The results correspond with those obtained by using the nitrometer. L. DE K.

**A New Colour Reaction of Thiophen.** By HANS KREIS (*Chem. Zeit.*, 1902, 26, 523).—A solution of thiophen in benzene or light petroleum mixed with a trace of *p*-methoxytetrahydroquinoline (thallin base) is shaken with two volumes of nitric acid of sp. gr. 1.4. The acid assumes the colour of methyl-violet, which disappears on dilution. A similar reaction is obtained with toluene containing methylthiophen. Most benzenes contain thiophen, which may be removed by treatment with sulphuric acid. L. DE K.

**Iodometry of Ferro- and Ferri-cyanides.** By ERWIN RUPP and ALBERT SCHIEDT (*Ber.*, 1902, 35, 2430—2434).—In order to replace de Haën's inexact method of estimating potassium ferrocyanide by means of standard permanganate, the quantitative conversion of ferrocyanide into ferricyanide by adding excess of a standard iodine solution and then titrating the excess of iodine by thiosulphate was tried; when the oxidation is carried out in the presence of sodium hydrogen carbonate, the method gives excellent results if the mixture of iodine and ferrocyanide is left for 15 minutes. In the presence of acetic acid, the oxidation only becomes complete when the mixture is warmed. With mineral acids, hydrogen iodide reduces ferricyanides. The authors have compared their method with Kistiakowsky's (*J. Russ. Phys. Chem. Soc.*, 1897, 29, 362), namely, titration with silver nitrate and potassium chromate as indicator, and have found that the results of both methods are in very good agreement. Potassium ferricyanide can be accurately estimated by reduction by means of ferrous sulphate to ferrocyanide and subsequent titration

of the latter by the above method ; hydrogen peroxide can also be used to reduce the ferricyanide, but the excess of the peroxide must be removed by boiling before the iodine is added. K. J. P. O.

**Estimation of Glycerol by means of Iodic Acid in presence of Sulphuric Acid.** By A. CHAUMEIL (*Bull. Soc. Chim.*, 1902, [iii], 27, 629—634).—For the purpose of estimating glycerol, the author employs iodic acid in presence of sulphuric acid, whereby iodine is liberated quantitatively and can be titrated with sodium thiosulphate. When the solution contains chlorides, which would be capable of interacting with the iodic acid, the chloride present is first determined by titration, and the corresponding amount of thiosulphate subtracted from the total amount used. A. F.

**Volumetric Estimation of Thymol.** By EMIL ZDAREK (*Zeit. anal. Chem.*, 1902, 41, 227—231).—A process similar to that of Koppeschaar for titrating phenol gives good results with thymol. The weighed substance is treated in a stoppered bottle with an excess of a standard bromide-bromate solution and hydrochloric acid. After shaking for five minutes, potassium iodide is added and the liberated iodine is titrated with thiosulphate. A return of the iodine-starch blue colour shortly takes place, but should be neglected. Under these conditions, the molecule of thymol consumes four atoms of bromine, but the tetrabromothymol is very unstable and could not be prepared in the dry state. The presence of alcohol does not affect the accuracy of the method. M. J. S.

**Reaction for Distinguishing  $\alpha$ -Naphthol from  $\beta$ -Naphthol.** By ARMAND JORISSEN (*Ann. Chim. anal.*, 1902, 7, 217—219).—A pinch of the sample is mixed in a test-tube with 2 c.c. of a solution of iodine in potassium iodide and then with excess of aqueous sodium hydroxide. On shaking the mixture,  $\beta$ -naphthol gives a clear, colourless liquid, but  $\alpha$ -naphthol yields a turbid solution of intense violet colour. Mixtures also give a more or less coloured solution. L. DE K.

**Estimation of Lactose in Milk.** By GUSTAVE PATEIN (*J. Pharm. Chim.*, 1902, [vi], 15, 505—509).—The variable results obtained in the estimation of lactose in milk are due to incomplete precipitation of proteids by such precipitants as the normal and basic acetates of lead. The acid solution of mercuric nitrate used by Patein and Dufau (*Abstr.*, 1902, ii, 291) is recommended for this purpose; the preparations so obtained can afterwards be used for check volumetric estimations of the lactose with Fehling's solution. T. A. H.

**Estimation of Sucrose in Preserved Fruits containing Starch Sugar.** By O. SCHREFELD (*Zeit. Ver. Deut. Zuckerind.*, 1902, 554, 204—206).—The official German method of estimating the proportion of sucrose in preserved fruits consists essentially in preparing a cold water extract of the fruit and weighing the amounts of copper reduced from Fehling's solution by this extract both before

and after inversion with hydrochloric acid. The amount of invert sugar corresponding with the difference between these two weights of copper is then ascertained by means of Wein's tables, and from this the sucrose present can be calculated. This method assumes that the reducing power of the inverted sucrose is not influenced by the presence of the starch sugar, but the author's experiments here described show that this is by no means the case. Since the proportion of dextrin in starch sugar varies widely, it is not possible to allow for its influence on the copper reduction by means of a formula. It is therefore recommended in such analyses to employ the optical inversion method, which should also be used for detecting the presence of starch sugar in sucrose.

T. H. P.

**Polarisation of Fruits, Jellies, Jams, and Honeys.** By L. M. TOLMAN (*J. Amer. Chem. Soc.*, 1902, 24, 515—524).—Hydrochloric acid increases the laevorotation of an invert sugar solution; the increase, other things being equal, is proportional to the quantity of acid used. Other things being equal and temperature varying, hydrochloric acid increases laevorotation by a definite percentage of the polarisation. In order to get a trustworthy result when using Clerget's formula for the calculation of the amount of sucrose in invert sugar, a correction should be made depending on the amount of hydrochloric acid present. On this point, reference should be made to the graphic representations in the original paper. All readings of the polariscope should be made at or about 20°.

L. DE K.

**Application of the Pentosan Process to Various Vegetable Matters and Materials used in the Manufacture of Paper.** By E. KRÖBER and CHARLES RIMBACH (*Zeit. angew. Chem.*, 1902, 15, 508—510).—Tables giving the amount of pentosan contained in a variety of substances as estimated by distillation with hydrochloric acid and treatment of the distillate with phloroglucinol. The following substances have been experimented with: sugar, potato-starch, Swedish filter paper, wadding, cotton-wool (none of these contains appreciable quantities of pentosan); various wood-gums (xylan); crude fibres from different materials prepared in different ways; various specimens of wood; fossil woods, lignite, coal (the latter yields no trace); various vegetable tissues including leaves, stems, roots, &c., the materials used in paper making, and also the finished article.

Provided the origin of the paper is known, its quantitative analysis is much assisted by a pentosan estimation owing to the great difference in pentosan yielded by the various constituents.

L. DE K.

**Estimation of Pentoses and Pentosans by means of Distillation with Hydrochloric Acid and Precipitation of the Furfuraldehyde with Phloroglucinol.** By E. KRÖBER and CHARLES RIMBACH (*Zeit. angew. Chem.*, 1902, 15, 477—482).—The authors have further improved this well known process. To obtain correct results, the weight of the phloroglucide (dried at 98°) should be increased by

0.0052 gram, this being the amount retained by the 550 c.c. of mother liquor and washings.

Tables are given for the calculation of the weight of the precipitate into furfuraldehyde, arabinose, araban, xylose, xylan, pentoses, or pentosans.  
L. DE K.

**Estimation of Hydrocyanic Acid.** By ANDREA ARCHETTI (*Chem. Zeit.*, 1902, 26, 555).—A definite volume of the sample is shaken with a weighed quantity ( $P$ ) of mercurous chloride, which then forms mercuric cyanide, hydrogen chloride, and free mercury; 1 mol. of mercurous chloride represents 2 mols. of hydrocyanic acid.

The undissolved mercurous chloride ( $p$ ) is collected on a filter and freed from the admixed mercury by washing with a mixture of 1 vol. of nitric acid of sp. gr. 1.40 and  $\frac{1}{2}$  volume of water. After it has been weighed, the amount of hydrocyanic acid is found by means of the formula ( $P-p$ ) 56/47.  
L. DE K.

**Iodometry of Thiocyanic Acid.** By ERWIN RUPP and ALBERT SCHIEDT (*Ber.*, 1902, 35, 2191—2195).—It is found that thiocyanic acid (and thiocyanates) can be accurately estimated by adding excess of  $N/10$  iodine solution to a dilute solution of a thiocyanate containing sodium hydrogen carbonate; after keeping for half-an-hour, the excess of iodine is titrated by means of  $N/10$  thiosulphate. The results show that 8 atoms of iodine are equivalent to 1 mol. of thiocyanic acid; the reaction is therefore expressed by the equation  $\text{KCNS} + 4\text{I}_2 + 4\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 6\text{HI} + \text{KI} + \text{ICN}$ . Since cyanogen iodide affects starch solution, the latter cannot be used as an indicator in titrating the excess of iodine; the disappearance of colour is depended on.

The estimation of a mixture of chloride and thiocyanate is effected by determining the total chloride and thiocyanate with silver nitrate by Volhard's process, and then titrating the thiocyanate with iodine. In the case of a mixture of cyanide and thiocyanate, the total is estimated by Volhard's method and the thiocyanate by iodine after the hydrocyanic acid has been removed by boiling the mixture with tartaric acid for 15—20 min. In a similar manner, a mixture of chloride, cyanide, and thiocyanate can be accurately analysed.

K. J. P. O.

**Estimation of Methyl Anthranilate in Ethereal Oils.** By ALBERT HESSE and OTTO ZIETSCHEL (*Ber.*, 1902, 35, 2355—2347. Compare Abstr., 1901, ii, 209, and Erdmann, this vol., ii, 292).—A comparison of the authors' method of estimating methyl anthranilate with that proposed by Erdmann. The latter process, although applicable to the pure ester, does not lend itself to the estimation of this compound in a complex mixture, the results being always too low. As indicated by the authors, it is preferable to first separate the ester by the action of sulphuric acid in ethereal solution.

Erdmann's method might, however, be employed with advantage in estimating the ester in the presence of methyl methylsalicylate, for both the ethereal salts would be precipitated together by the action of sulphuric acid.  
G. T. M.

**Determination of the Iodine Number.** By MORITZ KITT (*Chem. Zeit.*, 1902, 26, 554).—The author's process for preparing the Hübl solution (Abstr., 1901, ii, 587) has been found to answer in practice.

L. DE K.

**Estimation of Arachis Oil.** By MASSIMO TORTELLI and R. RUGGERI (*Chem. Centr.*, 1902, i, 833; from *Mon. sci.*, [iv], 16, 215—217. Compare Abstr., 1898, ii, 653).—According to Archbutt (Abstr., 1899, ii, 269), the melting point of the mixture of arachic and lignoceric acids obtained from pure arachis oil is between  $71^{\circ}$  and  $72.5^{\circ}$ , whilst the authors had previously found it to be  $74^{\circ}$ — $75.5^{\circ}$ . The discrepancy is probably due to the method used. Archbutt's method of partial precipitation of the soap with lead acetate, instead of using an excess, is according to the authors not so trustworthy as their own process.

L. DE K.

**Detection of Heated Milk.** By DU ROI and KÖHLER (*Milch-Zeit.*, 1902, 31, 17—18, 113).—Fifty c.c. of the milk are shaken with 1 c.c. of a 1 per cent. solution of hydrogen peroxide and 3 c.c. of the mixture then poured into a test-tube containing 3 c.c. of a solution of potassium iodide and starch. Should the milk be raw, a blue colour appears on thoroughly agitating the contents of the tube, whilst in the case of heated milk the mixture remains colourless. Heating the milk to  $80^{\circ}$  is sufficient to prevent the colour being formed. Small quantities of potassium dichromate or formaldehyde do not interfere with the reaction. Two per cent. of raw milk in heated milk can be detected by the test.

B. STORCH (*ibid.*, 81—82) prefers the use of a 2 per cent. aqueous solution of *p*-phenylenediamine instead of starch and potassium iodide, as the latter is liable to decomposition on keeping. He also uses a 0.2 per cent. solution of hydrogen peroxide.

FRANZ UTZ (*ibid.*, 145—146) mentions that the solution of hydrogen peroxide as used in the method described by du Roi and Köhler should not be stronger than 0.1 per cent. More concentrated solutions sometimes give a blue colour with starch and potassium iodide.

W. P. S.

**Detection of Heated Milk by Means of the Guaiacum Test.** By CARL ARNOLD and CURT MENTZEL (*Milch-Zeit.*, 1902, 31, 247).—When a 10 per cent. solution of guaiacum resin in acetone is allowed to run on to the surface of unheated milk, a blue zone appears at the junction of the two liquids. Boiled milk containing 12.5 per cent. of raw milk gives the blue coloration within 5 minutes, whilst boiled milk alone yields no colour, even after long standing. Acetone was found to be the best solvent for the guaiacum resin.

W. P. S.

**Use of the Refractometer in Milk Analysis.** By FRANZ UTZ (*Milch-Zeit.*, 1902, 31, 49—50).—The milk is allowed to curdle spontaneously at a temperature of  $37.5^{\circ}$  and filtered. The clear whey is then cooled to  $15^{\circ}$  and the refractive index taken. Genuine milk gave



numbers from 1.3431 to 1.3442, and when diluted with various quantities of water, the following numbers were obtained :

Added water.	Refraction at 15°.	Added water.	Refraction at 15°.
5 per cent.	1.3425—1.3430	33.3 per cent.	1.3401
10    ,,	1.3418—1.3425	40    ,,	1.3390—1.3393
20    ,,	1.3411—1.3412	50    ,,	1.3384—1.3388
25    ,,	1.3405	60    ,,	1.3373
30    ,,	1.3394—1.3403	Water alone	1.3373

The lactic acid in the whey has a very slight influence on the refractive index.  
W. P. S.

**Decrease in the Acidity of Milk.** By ARTHUR KIRSTEN (*Milch-Zeit.*, 1902, 31, 114—118).—The acidity of milk is stated to decrease when the milk is kept in open vessels and also when it is boiled or subjected to centrifugal action. This decrease is due to a loss of dissolved carbon dioxide. Carbon dioxide also accounts for a part of the acidity of fresh milk. The period of time during which the acidity of milk remains constant, termed the "incubation stage" by Soxhlet, should be considered, in the light of the author's experiments, as the time in which the lactic acid bacteria produce only so much lactic acid as is balanced by the loss of free carbon dioxide.  
W. P. S.

**Presence of Nitrates in Milk as an Indication of Adulteration.** By NICLAUS GERBER and P. WIESKE (*Milch-Zeit.*, 1902, 31, 82—84).—Nitrates may be tested for in milk by allowing a small quantity of the latter to run on to the surface of an equal volume of sulphuric acid containing a little formaldehyde. A blue or violet ring is formed, in the presence of nitrates, at the junction of the two liquids. As milk does not naturally contain any nitrates, the above test is of some use for detecting the addition of water to the milk, although most town water supplies are so free from nitrates that the test only occasionally yields positive results.  
W. P. S.

**Detection of Artificial Colouring Matters in Fresh and Sour Milk.** By M. WYNTER BLYTH (*Analyst*, 1902, 27, 146—151).—The action of decomposing milk on coal-tar dyes is the same as is the action of zinc dust and hydrochloric acid. The colour is destroyed and, although in some cases it may be restored by shaking with air, in others no re-appearance of the colour takes place. For the certain detection of added colouring matter, the following method is proposed. The milk is rendered faintly alkaline to litmus paper, evaporated to a paste, and thoroughly extracted with ether. The ethereal solution is evaporated to dryness, the residue of fat is extracted with water, and the residue obtained on the evaporation of the aqueous portion is tested for colouring matters. The fat-free milk residue is then exhausted with absolute alcohol, filtered, and separate portions of the alcoholic liquid evaporated in china basins. To the residues obtained, the usual tests may be applied. For instance, the sulphonated azo-dyes are recognised by the colour produced on adding

sulphuric acid; the natural colouring matters and non-sulphonated acid coal-tar dyes are soluble in ether, whilst the basic colours and sulphonated dyes are insoluble in this medium. W. P. S.

**Abnormal Milk.** By JULES WAUTERS (*Rev. intern. Falsific.*, 1902, 15, 67—69).—The milk from two cows in a herd of ten was found to be of very abnormal quality. One milk yielded from 1.319—2.575 per cent. of fat, 4.116—6.760 per cent. of casein and lactose, and 5.031—7.635 per cent. of non-fatty solids. The milk of the second cow gave 1.250—2.965 per cent. of fat, 5.190—7.110 per cent. of casein and lactose, and 6.190—8.085 per cent. of non-fatty solids. The ash of the milks was abnormally high. W. P. S.

**Estimation of the Soluble Acids in Butter.** By L. VANDAM (*Rev. intern. Falsific.*, 1902, 15, 61—65).—An estimation of the soluble acids in butter is stated to give more trustworthy indications of adulteration than are given by the Reichert-Wollny figure. Tables are given showing that the amount of soluble acids in some cases plainly pointed to adulteration, whilst the Reichert-Wollny figure was not unusually low. The estimation is particularly useful should cocoa-nut oil be present in the sample. W. P. S.

**Estimation of Glycine.** By EMIL FISCHER (*Zeit. physiol. Chem.*, 1902, 35, 229—230).—The author finds that glycine may be satisfactorily estimated by saturating at 0° with hydrogen chloride a solution of this amino-acid in absolute alcohol, thereby converting it into the hydrochloride of glycine ethyl ester, which separates, after standing at 0° for 12 hours, to the extent of 95 per cent. In presence of other amino-acids, the yield is less satisfactory (compare Fischer and Skita, *Abstr.*, 1901, i, 783). T. A. H.

**Estimation of Urea in Urine.** By CH. SALLERIN (*Bull. Soc. Chim.*, 1902, [iii], 27, 620—625).—The author has compared the methods of Mörner and Sjöqvist, of Salaskin and Zaleski, and of Braunstein (*Abstr.*, 1901, ii, 140) for the estimation of urea in urine, and finds that the method last mentioned is the best. For the complete hydrolysis of the urea, the author finds that it is necessary to heat the solution with phosphoric acid for seven hours at 150—155°. A. F.

**Jolles' Method of estimating Uric Acid.** By GABRIEL MÁTRAI (*Zeit. physiol. Chem.*, 1902, 35, 205—209).—Trustworthy results were not obtained in estimations of uric acid by the method described by Jolles. W. D. H.

**Estimation of Uric Acid in Urine.** By JULIUS RUDISCH and LEOPOLD BOROSCHEK (*J. Amer. Chem. Soc.*, 1902, 24, 562—569).—A modification of the silver method. One hundred c.c. of the sample are neutralised with a saturated solution of sodium carbonate, and 15 c.c. extra of this are then added. Ten c.c. of *N*/20 solution of silver chloride in saturated solution of sodium sulphite are added, and after standing

for an hour the precipitate is collected and washed with a dilute solution of sodium carbonate. The silver in the precipitate is then determined by the thiocyanate method. One atom of silver equals one molecule of uric acid. Small quantities of xanthine bases, which are also precipitated, may be allowed for by applying the principle of Salkowski's method (*Pflüger's Archiv*, 1898, 69, 280). L. DE K.

**Fractional Oxidation with the Aid of Indicators and its Application to the Estimation of Xanthine Derivatives in Urine.** By LADISLAUS NIEMIŁOWICZ (*Zeit. physiol. Chem.*, 1902, 35, 264—297).—When a solution of potassium permanganate is added to a liquid containing a series of substances of different stabilities towards this reagent, it is possible in certain cases to ensure the destruction of the least stable compound without losing more than traces of the most stable one. The point at which this occurs may be ascertained by titrating in presence of a coloured indicator, the stability of which towards permanganate is intermediate between those of the extreme members of the series present, and is also expressible in terms of permanganate necessary for its decolorisation. The author has devised two processes for the estimation of xanthine derivatives in urine involving the destruction of uric acid and the conservation of the xanthine compounds based on the principle already mentioned. To 100 c.c. of the sample, acidified by hydrochloric acid if necessary, 0.005 gram of indigo-carmin, dissolved in 1 c.c. of water, is added and the mixture titrated with permanganate until the green colour is just destroyed; this addition of indigo-carmin to the same sample and titration with permanganate is repeated until two consecutive titrations differ by not more than 0.1 c.c. (usually three titrations are necessary). At this point, the uric acid has been destroyed, but the xanthine compounds remain unattacked and may be estimated by the process devised by Denigès (*Abstr.*, ii, 1894, 403) or by that of Haycraft (*Abstr.*, 1886, 748). T. A. H.

**Error in the Estimation of Xanthouric compounds caused by certain Foods and Medicaments.** By GUSTAVE ANDRÉ (*J. Pharm. Chim.*, 1902, [vi], 15, 522—527).—The consumption of tea, coffee, and chocolate, or the employment of xanthine derivatives as medicinal agents, leads to an increased excretion in the urine of xanthouric compounds, which, by the usual analytical methods are calculated entirely as uric acid, and so give results of doubtful clinical value. T. A. H.

**Extraction of Alkaloids from Acid Solutions and of Alkaloid Salts from Aqueous Solutions.** By EDMUND SPRINGER (*Chem. Centr.*, 1902, i, 1064—1065; from *Apoth.-Zeit.*, 17, 225—226. Compare this vol., 390).—From the results of experiments on the extraction of alkaloids from acid solutions by treatment with chloroform in Gadamer's apparatus ("perforator") for half-an-hour, the following conclusions are drawn. Morphine, coniine, and nicotine are not extracted by the chloroform. Aconitine, strychnine, narcotine, quinine, and veratrine are extracted in considerable quantities in pre-

sence of hydrochloric acid of sp. gr. 1.12 and narcotine is also dissolved by chloroform in presence of sulphuric acid of sp. gr. 1.11. Traces of almost all the other alkaloids are removed from solutions containing hydrochloric acid or dilute sulphuric acid. Chloroform extracts considerable amounts of aconitine and narcotine, but only extremely small quantities of atropine and veratrine from solutions containing tartaric acid, whilst codeine, cocaine, and quinine do not dissolve under these conditions.

Phosphoric acid of sp. gr. 1.154, affects the behaviour of alkaloids to chloroform in the same way as sulphuric acid of sp. gr. 1.11, and, similarly, citric and oxalic acids resemble tartaric acid in this respect. In toxicological examinations, the presence of hydrochloric acid or of chlorides is therefore to be avoided; sulphuric and phosphoric acids are less harmful, but oxalic, citric, and tartaric acids may be more advantageously employed. The extraction of alkaloids is more complete in weak than in strong acid solutions, and is aided by the presence of large quantities of salts, but it is not affected by the presence of saponin, glycerol, &c. Morphine hydrochloride and sulphate and quinine sulphate are not removed from aqueous solutions by chloroform, but traces of cocaine are extracted from aqueous solutions of its hydrochloride; other alkaloids are dissolved in considerable quantities partly as free base and partly as salt.

E. W. W.

**Limits of Sensitiveness of Alkaloidal Precipitants.** By EDMUND SPRINGER (*Chem. Centr.*, 1902, i, 1027; from *Apoth.-Zeit.*, 17, 201—202).—Salts of the alkaloids are more readily precipitated from a dilute solution than are the alkaloids themselves. The most delicate precipitants are phosphomolybdic acid and potassium bismuthiodide.

L. DE K.

**Microchemical Detection of Some Alkaloids.** By SURRE (*Bull. Soc. Chim.*, 1902, [iii], 27, 626—629).—The solution containing the alkaloid is placed on a watch-glass, and to it are added a drop of the particular reagent and a few drops of absolute alcohol; the crystals formed are then examined under the microscope. The following results have been obtained:—With Mayer's reagent: strychnine: slender needles, single or grouped, in the form of X or Y; with polarised light, they show a faint bluish tinge. Codeine: small tufts of crystals of a bright silver-white colour with polarised light. With Bouchardat's reagent: Brucine: crystals in the form of plumes; with artificial polarised light, bright yellow, blue, and red. Atropine: short, thick, dark brown crystals; with polarised light, dark orange-coloured. Hyoscyamine: crystals closely resembling those of atropine. With Marmé's reagent: Morphine: long, silky, thread-like crystals. Papaverine: very short crystals grouped in large numbers round a common point; with polarised light, whitish pink. Sparteine: fern-like crystals growing from a common axis. The following alkaloids do not crystallise under the foregoing conditions: narcotine, narceine, thebaine, quinine, quinidine, veratrine, cinchonine, cinchonidine, hyoscyne, aconitine, cocaine, nicotine, cicutine, caffeine, theobromine,

pilocarpine, curarine, and some others. The above method cannot be employed in the presence of ptomaines. A. F.

**Estimation of Indigotin in Fabrics.** By A. BINZ and F. RUNG (*Zeit. angew. Chem.*, 1902, 15, 557—559).—The authors state that both commercially pure and chemically pure indigotin suffer a slight decomposition when boiled with glacial acetic acid in the presence of woolly substances. This does not, however, interfere with the use of glacial acetic acid as a solvent when making comparative analytical experiments with fabrics containing indigo. L. DE K.

**Reaction for Santonin in Urine.** By ED. CROUZEL (*Ann. Chim. anal.*, 1902, 7, 219—220).—It is known that urine from a person to whom santonin has been administered turns red on adding alkalis or ammonia. The author states that the test is rendered more delicate by using calcium hydroxide, or better still, calcium carbide.

The test does not work with urine in which santonin has been simply dissolved, but only when this has been taken internally. The urine turns a deep yellow, milky colour, and the test may be obtained even 60 hours after taking a dose of santonin. The reaction may probably be useful in the study of kidney diseases. L. DE K.

**Colour Reactions of Red Blood-corpuscles in Diabetes.** By J. LE GOFF (*Compt. rend.*, 1902, 134, 1119—1120).—If a film of normal blood is treated with a mixture of eosin and methylene-blue, the red corpuscles are stained with the eosin; if the blood is diabetic, they take up the methylene-blue. After removal of the hæmoglobin, these differences do not obtain. Normal blood mixed with dextrose, lævulose, xylose (but not with sucrose), aldehyde, or acetone, shows the same affinity of the red corpuscles for basic dyes. W. D. H.

NOTE.—The main fact described above is not a new discovery; it is usually described as Williamson's reaction. W. D. H.

**Volumetric Estimation of Sodium Methylarsenate.** By ELIE FALIÈRES (*J. Pharm. Chim.*, 1902, [vi], 15, 466—469).—Although silver methylarsenate,  $\text{CH}_3\cdot\text{AsO}_3\text{Ag}_2$ , is slightly soluble in water, it becomes practically insoluble in presence of excess of silver nitrate. For the purpose of estimating sodium methylarsenate,  $\text{CH}_3\cdot\text{AsO}_3\text{Na}_2\cdot 6\text{H}_2\text{O}$ , the solution of this salt is treated with a known excess of silver nitrate, the solution filtered from the insoluble silver methylarsenate and the filtrate titrated with a standardised solution of sodium chloride. A. F.

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## General and Physical Chemistry.

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**Comparative Study of the Spectra, Densities, and Melting Points of some Groups of Elements, and of the Relation of Properties to Atomic Mass.** By HUGH RAMAGE (*Proc. Roy. Soc.*, 1902, 70, 1—27).—The author arrives at the following conclusions. The properties of the elements are fundamentally due to the structure of the atoms as revealed by their spectra rather than to the quantity of matter in them. Considering that the strontium molecule must have a similar structure to the calcium molecule, it is inconceivable that, in the genesis of the elements, the transition from calcium to strontium proceeded through the intermediate elements. In the case of the elements tellurium and iodine, with neighbouring atomic weights, the genesis was not from tellurium to iodine, but from or through oxygen and fluorine respectively. It is probable that in the genesis of the elements the properties of certain fundamental substances are modified by successive additions of matter, or by causes of which this is the apparent result. The regularity in the changes in the properties of lithium, beryllium, boron, and carbon, as shown by the diagrams communicated, is very remarkable and suggestive, for the changes in properties are approximately proportional to the quantity of matter in the atom in excess of a constant (about 6), as if it were the same matter that is added in each case.

J. C. P.

**Chemical Dynamics and Statics under the Action of Light.** By MEYER WILDERMAN (*Proc. Roy. Soc.*, 1902, 70, 66—74).—With the object of elucidating the laws that govern chemical equilibrium in light, the author has studied the progress of the reaction  $\text{CO} + \text{Cl}_2 = \text{COCl}_2$ . The extent to which carbon monoxide and chlorine have united can easily be determined, because the reaction is accompanied by a gradual change of volume. To secure a powerful light of steady composition, acetylene was used, and with the help of a thermopile and galvanometer the intensity could be adjusted to about 0.1 per cent. As the slightest traces of air or water-vapour markedly retard or accelerate the combination of carbon monoxide and chlorine, the greatest care had to be taken in the preparation of these gases. The velocity of combination of carbon monoxide and chlorine is found to be adequately represented by the differential equation  $dx/dt = K(A-x)(B-x)$ , where  $A$  and  $B$  are the initial quantities of carbon monoxide and chlorine, measured by their partial pressures,  $A-x$  and  $B-x$  are the quantities present after time  $t$ , and  $K$  is a constant for light of a given wave-length and steady intensity. In discussing evidence from the above and similar cases of chemical reaction in homogeneous systems, the author concludes that chemical equilibrium in homogeneous systems is regulated, in the light as well as in the dark, by the laws of mass action. The author deals also with the phenomena of chemical induction and deduction, as well as with induction and deduction periods of energy.

J. C. P.

**Conditions Determinative of Chemical Change and of Electrical Conduction in Gases, and on the Phenomena of Luminescence.** By HENRY E. ARMSTRONG (*Proc. Roy. Soc.*, 1902, 70, 99—109).—The author regards Brereton Baker's recent work as confirmatory of his own view that the presence of an electrolyte is a necessary condition for the occurrence of chemical action, and that pure gases should be perfect dielectrics (see Armstrong, *Proc.*, 1893, 145, and *Trans.*, 1895, 1141).

The problem of electrical discharge in gases has not yet been attacked with the same accurate methods as have been applied by Dixon, Brereton Baker, and Shenstone in the case of chemical change, and the author contends that there is evidence that the discharge in a vacuum tube is conditioned by the presence of impurities (from soft glass, sulphuric acid, and commercial phosphoric oxide).

In the case of the luminosity of the rare earths, the incandescence of oxides generally, and the phenomena of phosphorescence under the influence of the electric discharge, it is argued that the process in each case may be one of recurrent oxidation or polymerisation. The argument is extended to the case of emanations from radioactive substances, and to that of the 'so-called' ionisation of air.

J. C. P.

**Researches on Elements founded on the Reciprocal Action of Two Liquids.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1902, 134, 1461—1478. Compare this vol., ii, 375, 376).—The amount of hydrogen evolved per minute in a voltameter when a current was passed through it was measured. In the circuit of the current, a known metallic resistance was interposed. Using two Daniell cells and with the voltameter under the ordinary atmospheric pressure, there is no visible evolution of gas when there is a resistance of 5000 ohms in the circuit. If the resistance is reduced to 2000 ohms, the gas evolution commences, and 0.000187 mg. of hydrogen is evolved per minute. At 1000 ohms, the quantity of hydrogen is 0.00037 mg. The pressure in the voltameter was reduced to 5 mm., and the gas evolution then becomes apparent when the resistance is 25,000 ohms. At 20,000 ohms, the hydrogen evolved per minute amounts to 0.000018 mg.

The evolution of gas is produced with a smaller *E.M.F.* if the voltameter contains a substance, such as pyrogallol, capable of absorbing oxygen—a fact which is probably due to the diminution of polarisation.

Using two Daniell cells and with pyrogallol in the voltameter, the evolution of gas is apparent when there is a resistance of 20,000 ohms in the circuit, and 0.000044 mg. of hydrogen is evolved per minute. With 10,000 ohms, the quantity of hydrogen amounts to 0.000087 mg. Employing a single Daniell cell and with the pressure in the voltameter (containing pyrogallol) reduced to 5 mm., the evolution becomes apparent when the circuit contains a resistance of 90,000 ohms. From these numbers, it is evident that the presence of pyrogallol exercises a profound influence on the evolution of gas in the voltameter.

A number of cells previously examined (*loc. cit.*) have been re

investigated. It is now found that the *E.M.F.* varies slightly with time, showing at first a slight increase, and different cells of the same composition give a slightly different *E.M.F.* After resting for some time, however, the cell gives an approximately constant *E.M.F.* These deviations are attributed to the state of humidity of the atmosphere, which interferes with the insulation.

With a battery of six elements composed of 0.2*N* sulphuric acid and 0.2*N* sodium hydroxide in porous vessels, the *E.M.F.* immediately after setting up was 2.94 volts. After the circuit with an external resistance of 4000 ohms had been closed for 4 minutes, the *E.M.F.* fell to 1.98 volts. The circuit was then broken for 15 minutes; the *E.M.F.* again rose to 2.58 volts, and after being closed for 4 minutes it decreased to 1.56 volts. After 7 minutes, the circuit being open, the *E.M.F.* had risen to 1.92 volts, and at the end of an hour to 2.46 volts. Closing the circuit for 7 minutes caused the *E.M.F.* to sink to 1.68 volts, and then opening it for 1 minute brought about a rise to 1.74 volts. By this time, the titre of the sodium hydroxide had decreased by 7 per cent. Thirty-six hours after setting the apparatus together, it was found that the alkali was completely neutralised and no current could be obtained. The same solutions have been examined when contained in separate vessels connected by a syphon; similar results have been obtained. Also with others of the solutions previously studied, analogous results have been found. These results prove that the elements examined are capable of yielding a continuous current.

The number of elements required to give a visible evolution of gas in the voltameter can be ascertained from the formula

$$i = (N - 1.6) / (2.10N\epsilon / n - R),$$

where *i* is the intensity expressed in amperes,  $\epsilon$  the *E.M.F.* of one element, *N* $\epsilon$  that of *N* elements in series, *n* the number of scale-divisions over which the galvanometer needle moves, and *R* the external resistance. The values calculated from this formula agree well with the results previously found. J. McC.

**Evident Electrolytic Actions developed by Elements constituted by the Reactions between Two Liquids, one containing an Acid, the other an Alkali.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1902, 135, 129—133).—It is shown that an element consisting of an acid and an alkali in porous vessels is capable of giving a definite *E.M.F.* The current developed is continuous, and with 6 elements containing hydrochloric acid and sodium hydroxide 2.4 volts can be obtained. With the aid of these elements, acidified water can be electrolysed, and if pyrogallol be added the evolution of gas is evident, particularly if the voltameter be under reduced pressure. J. McC.

**Correction of Observed Values of Specific Heats and Heats of Vaporisation of Organic Compounds of High Boiling Point.** By WLADIMIR F. LUGININ (*Ann. Chim. Phys.*, 1902, [vii], 26, 228—247. Compare Abstr., 1899, ii, 269, and 1901, ii, 145).—By means of an improved form of apparatus described in the *J. de Physique* (1901, [iii], 10, 5), the author has obtained exact



values of the specific heats and heats of vaporisation of the following organic substances :

	Latent heat of vaporisation.	Specific heat.	Temperature interval.
Methyl hexyl ketone.....	71.11	0.5723	172° - 23°
Ethylene glycol .....	190.90	0.6808	195 - 20
Benzyl alcohol .....	98.46	0.5579	200 - 22
Benzaldehyde .....	86.55	0.4453	172 - 22
Diethyl oxalate .....	67.58	0.4818	180 - 21

The application of Trouton's law,  $MS/T = K$ , to these data shows that diethyl oxalate, benzaldehyde, and methyl hexyl ketone do not exhibit polymerism in the liquid state, whilst the presence of polymeric molecules is distinctly noticeable in the case of ethylene glycol, but only just appreciable in that of benzyl alcohol.

G. T. M.

**Specific Heats and Heat of Vaporisation of the Paraffin and Methylene [*cyclo*Paraffin] Hydrocarbons.** By CHARLES F. MABERY and ALBERT H. GOLDSTEIN (*Amer. Chem. J.*, 1902, 28, 66-78).—The specific heats of a number of hydrocarbons of the paraffin and *cyclo*-paraffin series were determined by means of a Bunsen ice calorimeter. The following results were obtained :

Hydrocarbon.	$C_6H_{14}$ .	$C_7H_{16}$ .	$C_8H_{18}$ .	$C_9H_{20}$ .	$C_{10}H_{22}$ .	$C_{11}H_{24}$ .	$C_{12}H_{26}$ .	$C_{13}H_{28}$ .
Boiling point	68°	91°	98°	125°	151°	162°	172°	195°
Specific heat.	0.5272	0.5005	0.5074	0.5052	0.5034	0.4951	0.5021	0.5013
K.....	2.26	—	2.21	2.21	2.22	—	2.23	2.23

Hydrocarbon.	$C_{12}H_{26}$ .	$C_{13}H_{28}$ .	$C_{14}H_{30}$ .	$C_{15}H_{32}$ .	$C_{16}H_{34}$ .	Com- mercial gasoline.	Crude Ohio petroleum.
Boiling point	214°	226°	242°	260°	275°	—	—
Specific heat.	0.4997	0.4986	0.4973	0.4966	0.4957	0.5135	0.4951
K.....	2.23	2.24	2.23	2.24	2.23	—	—

Hydro- carbon.	$C_6H_{12}$ .	$C_7H_{14}$ .	$C_8H_{16}$ .	$C_9H_{18}$ .	$C_{10}H_{20}$ .	$C_{11}H_{22}$ .	$C_{12}H_{24}$ .	$C_{13}H_{26}$ .	$C_{14}H_{28}$ .	$C_{15}H_{30}$ .
Boiling point.	68°	98°	119°	135°	160°	190°	212°	232°	244°	263°
Specific heat.	0.5062	0.4879	0.4863	0.4851	0.4692	0.4819	0.4570	0.4573	0.4531	0.4708
K .....	2.26	2.28	2.37	2.27	—	2.25	—	—	—	2.20

These results show that there is a uniform decrease in specific heat with increase in molecular weight, and also that the normal hydrocarbons, such as heptane (b. p. 98°) and decane (b. p. 172°) have higher specific heats than their isomerides, such as *is*oheptane (b. p. 91°) and *is*odecane (b. p. 162°). The constant K (sp. heat  $\times$  mol. weight/number of atoms in molecule) for the paraffin series is 2.23, whilst in the case of the *cyclo*paraffin hydrocarbons the mean value is seen to be somewhat higher.

The specific heats of a series of hydrocarbons separated from the high-boiling portion of Pennsylvania petroleum gave the following values :

Hydrocarbon.	$C_{16}H_{32}$ .	$C_{18}H_{36}$ .	$C_{20}H_{40}$ .	$C_{23}H_{46}$ .	$C_{24}H_{48}$ .
Boiling point .....	173°	202°	223°	260°	272°
Specific heat .....	0·4723	0·4723	0·4706	0·4612	0·4586

The following are the specific heats of hydrocarbons separated from Texas petroleum :

Hydrocarbon.	$C_{14}H_{26}$ .	$C_{15}H_{28}$ .	$C_{16}H_{30}$ .	$C_{21}H_{38}$ .	$C_{25}H_{46}$ .
Boiling point under 50 mm. ...	127°	142°	162°	218°	273°
Specific heat .....	0·4447	0·4439	0·4426	0·4560	0·4650
K.....	2·15	2·15	2·14	—	—

The two last results are not trustworthy, since the quantities of the hydrocarbons were very small and the oils begin to crystallise at 0°.

The specific heat was also determined in the following crude oils from various fields; the results indicate that the specific heat of crude oils is an important property from a practical point of view :

	Texas								Com-
Oil.	Pennsyl- vania.	Berea grit.	Japan- ese.	(Lucas well).	Rus- sian.	Wyom- ing.	Cali- fornia.	Texas.	mercial Ohio.gasoline.
Sp. gr.	0·8095	0·7939	0·8622	0·9200	0·9079	0·8816	0·9600	0·9466	—
Specific heat.	0·5000	0·4690	0·4532	0·4315	0·4355	0·4323	0·3980	0·4009	0·4951

The heats of vaporisation of certain hydrocarbons were determined by means of the apparatus devised by Kahlenberg (*J. Physical Chem.*, 1901, 5, 215). The following results show a rapid decrease in the latent heat with increase in the molecular weight :

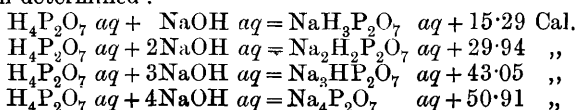
Hydrocarbon.	Hexane.	Heptane.	Octane.	Hexa- methyl- ene.	Dimethyl- penta- methyl- ene.	Methyl- hexa- methyl- ene.	Dimethyl- hexa- methyl- ene.
Boiling point ...	68°	98°	125°	68—70°	90—92°	98°	118—119°
Heat of vaporisa- tion (calories)..	79·4	74·0	71·1	87·3	81·0	75·7	71·7

E. G.

**Hydration of Zinc Oxide.** By ROBERT DE FORCRAND (*Compt. rend.*, 1902, 135, 36—39).—Zinc oxide prepared at 125° combines with water forming the crystallised hydroxide,  $Zn(OH)_2$ , with development of + 2·19 Cal. (liquid water). The oxide prepared at a bright red heat, which is probably more or less polymerised, absorbs water in a moist atmosphere, forming hydroxides of different condensation, the heat developed per mol. of water being from 4·5 Cal. to 5·0 Cal. Similar results are obtained with the hydroxide prepared by precipitation. The condensation of  $nZn(OH)_2$  into  $[Zn(OH)_2]_n$  develops about  $n \times 3·8$  Cal.

C. H. B.

**The Acidity of Pyrophosphoric Acid.** By H. GIRAN (*Compt. rend.*, 1902, 134, 1499—1502).—The following heats of neutralisation have been determined :

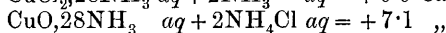


Neutralisation by the first mol. of sodium hydroxide evolves 15.29 Cal.; by the second mol. 15.65 Cal.; by the third mol. 13.11 Cal.; and by the fourth mol. 7.86 Cal. Pyrophosphoric acid is therefore a tetrabasic acid.

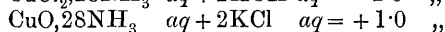
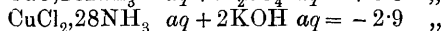
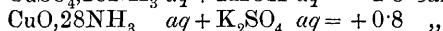
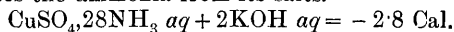
Solid pyrophosphoric acid was obtained by decomposing silver pyrophosphate with dry hydrogen chloride. Its heat of solution is +7.78 Cal. Since the heat of solution of syrupy pyrophosphoric acid is +10.22 Cal., it follows that this latter is in a superfused condition, its heat of fusion being -2.44 Cal.

Sodium trihydrogen pyrophosphate, prepared by the action of syrupy pyrophosphoric acid on disodium dihydrogen pyrophosphate at 100°, has heat of solution +0.67 Cal. The heats of solution of disodium dihydrogen pyrophosphate, trisodium hydrogen pyrophosphate, and tetrasodium pyrophosphate are respectively -2.18 Cal., +6.77 Cal., and +11.85 Cal. The difference in the heats of solution indicates that the salts are true compounds and not mixtures. J. McC.

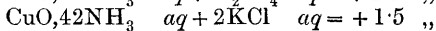
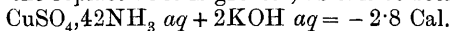
**Displacement of Strong Bases by Ammoniacal Cupric Oxide.** By ALBERT BOUZAT (*Compt. rend.*, 1902, 134, 1502—1505. Compare this vol., ii, 502).—The thermochemical action of solutions of ammoniacal cupric oxide on solutions of ammonium, potassium, and calcium salts has been measured:



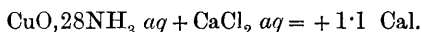
The difference between the actions is almost the same as that between the heats of neutralisation of the ammoniacal cupric hydroxide and ammonia (7.2 Cal.), consequently the complex base almost completely replaces the ammonia from its salts.



From these results, it is evident that the complex radicle partially replaces the potassium from its salts. In more concentrated ammoniacal solution, the replacement is greater, as can be seen from:



That the acid distributes itself between the two bases is proved by the fact that an ammoniacal cupric salt solution acquires the power of dissolving cellulose when potassium hydroxide is added, and cellulose is deposited from a solution of ammoniacal cupric hydroxide when a potassium salt is added. Cellulose is only soluble in a solution of the free base.



In this case also there is an equilibrium established between the amounts of base distributed between the acid, and in more concentrated ammoniacal solution the quantity of calcium replaced is so great that lime is precipitated.

The ammoniacal cupric hydroxide is to be regarded as a fairly strong base. J. McC.

**Heat of Dilution of Sodium Sulphate.** By ALBERT COLSON (*Compt. rend.*, 1902, 134, 1496—1497).—The point at which  $A = f(t) = 0^\circ$ , where  $t$  is the initial temperature of the solution, has been determined for solutions containing 200 grams of sodium sulphate in 100, 300, 500, 700, and 750 c.c. of water respectively. The points found were:  $59.5^\circ$ ,  $59.5^\circ$ ,  $57^\circ$ ,  $52^\circ$ , and  $52-53^\circ$ . J. McC.

**Theory of the Critical Phenomena and Vaporisation: Theory of Solution.** By ISODOR TRAUBE (*Ann. Physik.*, 1902, [iv], 8, 267—311).—The author gives an historical account of the study of the critical temperature and calls special attention to the apparent anomalies noticed by Ramsay, de Heen, Jamin, Mathias, Batelli, Guye, Dwelshauvers-Dery, and Galitzin. Ramsay observed phenomena which indicate that in a sealed tube above the critical temperature diffusion takes place, whilst de Heen and Dwelshauvers-Dery's experiments show that the density of a substance is not uniform about the critical temperature. These observations have been confirmed. A U-tube containing ether was heated for half-an-hour to  $10^\circ$  above the critical temperature, and on cooling it was observed that one limb filled with a cloud, whilst the other remained perfectly clear, and even above the critical temperature there was a visible meniscus at the low end of the tube quite like the meniscus of a liquid.

These observations lead the author to conclude that the view that the critical temperature is the point above which a substance can only exist in the gaseous condition is incorrect. The values of  $b$  in van der Waals' equation for non-associated liquids increase with rising temperature, the increase being greatest near the critical temperature. The value of  $b$  at the critical temperature is  $v_K/3$ ; it is shown that  $b$  increases even after the critical temperature has been reached, and it is to this change of  $b$  in passing from the liquid to the gaseous state that the anomalous observations referred to are attributed. At the critical temperature and at corresponding temperatures, the constant  $b$  and the co-volume  $v - b$  are proportional; consequently at the critical temperature the total volumes and the covolumes of a gasogenic and a liquidogenic molecule are in the same ratio as the gasogenic and liquidogenic constants  $b$ .

The author supposes that the increase in volume undergone by the atoms of a complex molecule during rise of temperature is not gradual but sudden. He assumes that there are two kinds of molecules—gasogenic and liquidogenic. These mutually dissolve each other and the amount of each present in any particular phase is conditioned by the temperature.

Van der Waals (*Abstr.*, 1901, ii, 644) has arrived at practically the same conclusion.

Liquids above absolute zero are solutions of gasogenic in liquidogenic molecules; these are in mobile equilibrium, but it requires a certain time for the establishment of this equilibrium. The critical temperature appears then as a triple point at which gasogenic and liquidogenic particles are completely miscible. When this is represented on a system of coordinates, using the value of  $b$  as ordinate and temperature as abscissa, the curve cuts the temperature axis at a

point above the critical temperature, which corresponds with the temperature above which only gasogenic particles can exist; for this point the term *absolute gasification point* is suggested.

According to this hypothesis, the whole of the pressure-volume curve for a substance at its critical temperature becomes realisable; the increase of volume with rising pressure is due to the passage from the liquidogenic to the gasogenic condition. It is shown that the volume of the gasogenic particle is almost twice that of the liquidogenic, and this is nearly the same for all substances.

It has been assumed that the heat of vaporisation at the critical temperature is zero; but Villard's experiments do not confirm this, and it is shown that according to the above hypothesis the heat of vaporisation at the critical temperature is  $0.41 T_c dp/dT v_c$ , where  $T_c$  is the critical temperature, and  $v_c$  the critical volume.

The relative quantities of liquidogenic and gasogenic particles at any particular temperature can be calculated as well as the heat of gasogenisation. At the normal boiling points, all solvents contain about the same proportion of gasogenic particles, namely, about 9 per cent. This leads to a discussion of the theory of solution; it is assumed that the dissolved substance influences the gasogenic particles, and thus by decreasing the proportion of them, hinders gasification and consequently raises the boiling point. The vapour pressure, the freezing point, and the osmotic pressure are influenced in the same way, and therefore van't Hoff's laws follow from the hypothesis. Electrolytes are assumed to influence twice the number of gasogenic particles that non-electrolytes do, and the author rejects the theory of Arrhenius and supports the older Clausius' assumption of continuous dissociation and association of the dissolved particles. J. McC.

**Simultaneous Distillation of Two Non-miscible Substances.** By EUGÈNE CHARABOT and J. ROCHEROLLES (*Compt. rend.*, 1902, 135, 175—177).—When the value of  $P/P'$  is less than unity,  $P$  being the weight of non-miscible liquid which distils and  $P'$  the weight of water, this ratio increases as the temperature rises (by increasing the pressure). On the other hand, when the value of  $P/P'$  is greater than 1, it decreases as the temperature is increased. These conclusions have been experimentally confirmed in the former case with limonene, geraniol, citronellol, and methylheptenone, and in the latter with pinene, benzene, isopentane, *n*-hexane, and carbon tetrachloride. J. McC.

**Diffusion of Hydrogen through Platinum.** By ADOLF WINKELMANN (*Ann. Physik.*, 1902, [iv], 8, 388—404. Compare Abstr., 1901, ii, 646).—Platinum has been examined in the same way that palladium was. The rate of diffusion of the hydrogen increases after the platinum has been heated for some time. It is proved that this is not due to expulsion of occluded air, but to the crystalline structure assumed by the metal. When the platinum has passed into this state it persists therein.

The diffusion of hydrogen through red-hot platinum is not proportional to the pressure of the gas, but it is probable that the diffusion

is accompanied by a dissociation of the molecules, and only the atoms of hydrogen pass through the metal. The results obtained agree well with the formula given previously.

The experiments were made with a platinum tube 19 cm. long, 1 mm. in diameter, and 0.1 mm. thick in the walls. The metal was heated electrically.

J. McC.

**Preparation of Cells for the Measurement of High Osmotic Pressures.** By HARMON N. MORSE and J. C. W. FRAZER (*Amer. Chem. J.*, 1902, 28, 1—23).—In a previous paper (Morse and Horn, *Abstr.*, 1901, ii, 543), a method was described for the electrolytic deposition of an osmotic membrane in the wall of a porous cell. The highest pressure which had then been reached with such a cell was 4.5 atmospheres, the inability to withstand higher pressures being due, not to the weakness of the membrane, but to the difficulty of securing the manometer in the cell. The present paper gives an account of improved arrangements for securing the manometer, and of certain modifications in the construction of the cell. By means of the improved apparatus, with a normal solution of sugar, a pressure of 31.5 atmospheres has been attained. The osmotic pressure of a seminormal solution of sugar at 20° was found to lie between 13 and 14 atmospheres. For details, the description and diagrams in the original must be consulted.

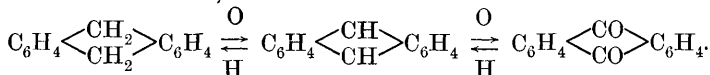
E. G.

**Classification of the Elements.** By HENRY E. ARMSTRONG (*Proc. Roy. Soc.*, 1902, 70, 86—94).—On the assumption that the 'elementary difference' is about a unit, the elements are arranged in sixteen vertical series, the first horizontal period closing with oxygen. The molecule of argon is assumed to be diatomic, and that element appears immediately after fluorine; this position is in harmony with the author's view that argon is an element of intense activity, the molecule exhibiting no residual affinity, because the component atoms so completely satisfy each other. The atomic weight 77 is assigned to selenium, so that it may appear in the oxygen-sulphur group. It is not always possible, as it is in the first and second periods, to proceed by units; thus, in the third period, after scandium, it is necessary to step down five units to bring titanium into position. In the fourth period, iron and nickel both appear in the fourth column in order to bring copper into a suitable position. The chief point brought out by this mode of classification is the existence of groups of elements from the highest term of which alone 'progression' takes place. It is probable that when atomic weights are more accurately known, such grouped elements will be found only in columns 4, 8, and 12.

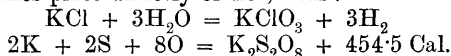
J. C. P.

**Suggested Modifications of the Sign of Equality for use in Chemical Notation.** By HUGH MARSHALL (*Proc. Roy. Soc. Edin.*, 1902, 24, 85—87).—The symbol  $\rightleftharpoons$  is used for a double purpose: (1) to indicate that a reaction is reversible; (2) to indicate, especially in organic chemistry, the stages by which one substance may be obtained from another. To avoid this double use, the author makes the following suggestions:

(1) The use of the symbol  $\rightleftharpoons$  should be restricted to the second case referred to above, thus:

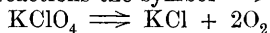


(2) The ordinary symbol  $=$  should be used only in equations required for purposes of calculation, irrespective of whether the change represented takes place directly or not, thus:

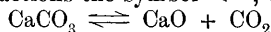


(3) In writing a complete equation, corresponding with some actual chemical change, singly-barbed arrows should be used, subject to the following modifications:

(a) for irreversible reactions the symbol  $\Rightarrow$ , thus:

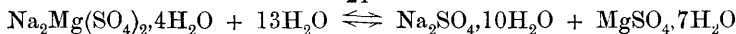


(b) for reversible reactions the symbol  $\rightleftharpoons$ , thus:

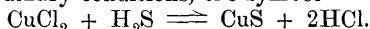


(c) for reversible reactions associated with a definite transition

temperature, the symbol  $\xrightleftharpoons[t^\circ]{t^\circ}$  or  $\xrightleftharpoons[21^\circ]{}$ , thus:



(d) for cases where reversible reactions go almost completely in one direction under ordinary conditions, the symbol  $\Rightarrow$ , thus:



J. C. P.

**Principal and Supplementary Valencies and the Constitution of Ammonium Compounds.** By ALFRED WERNER (*Annalen*, 1902, 322, 261—296).—A theoretical communication enunciating the author's theories of valency, and containing a summary of the various views held at different periods on this subject.

An attempt is made to distinguish between two forms of valency. Principal valency ("Hauptvalenz") is the capacity for combination possessed by elementary or compound radicles which are either capable of existing in the ionised condition or which are equivalent to these ions. Supplementary valency ("Nebervalenz") is the affinity by virtue of which radicles which do not exist in the ionised condition can combine with one another.

For example, the following radicles,  $-\text{Cl}$ ,  $-\text{Na}$ ,  $-\text{NO}_2$ , and  $-\text{CH}_3$  possess principal valency, whilst the complexes,  $-\text{OH}_2$ ,  $-\text{NH}_3$ ,  $-\text{ClK}$ , and  $-\text{CrCl}_3$  enter into combination by virtue of their supplementary valency.

It is not always possible to differentiate between these two forms of valency, and in all probability they differ in degree rather than in kind.

The number of radicles which can combine with any given central element depends on the available space within this atom's sphere of influence rather than on the nature of the combining radicles. In the case of carbon, the maximum number of dependent radicles is undoubtedly four. Many other elements appear capable of combining with six radicles. The series  $[\text{Pt}(\text{NH}_3)_6]\text{X}_4$ ,  $(\text{PtCl}_6)\text{R}_2$ ,  $[\text{Pt}(\text{SCN})_6]\text{R}_2$  and

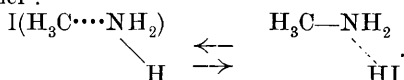
$(\text{PtBr}_6)\text{R}_2$ , indicate that this is the maximum number ("coordination constant") in the case of platinum. The complex thus formed, however, still possesses residual affinity, and this is satisfied by combination with the radicle R in a second sphere of influence.

In general, the capacity for combination of an atom is determined by three factors, principal valency, supplementary valency, and the coordination constant.

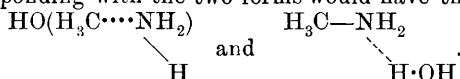
These hypotheses are employed in discussing the constitution of ammonium compounds.

It is pointed out that the theory which supposes that the hydrogen and chlorine of ammonium chloride are independently attached to the nitrogen does not account for the great difference in stability between the partially and completely substituted quaternary ammonium hydroxides. As an alternative hypothesis, the author suggests that the combination of ammonia and hydrogen chloride is due to the supplementary valency or residual affinity of the nitrogen and the acidic hydrogen, and ascribes to ammonium chloride the coordination formula  $\text{H}_3\text{N}\cdots\text{H}\cdot\text{Cl}$ , the supplementary valency being indicated by the dotted line. The corresponding formula for ammonium hydroxide is  $\text{H}_3\text{N}\cdots\text{H}\cdot\text{OH}$ . These formulæ account for the electrochemical behaviour of the compounds in aqueous solution, the salt, which still contains the chlorine ion attached to hydrogen, being strongly ionised, whilst the base resembles its prototype, water, in exhibiting an abnormally small ionisation.

The combination of methyl iodide and ammonia is supposed to result in the formation of the complex  $\text{I}(\text{H}_3\text{C}\cdots\text{NH}_3)$ , but, since the same compound is produced from hydrogen iodide and methylamine, it is probable that, in the former process, rearrangement occurs in the following manner:



Possibly the iodide contains the two forms in a state of dynamic equilibrium; the first modification is termed the "carbonium form," whilst the latter is referred to as the "hydronium form." The hydroxides corresponding with the two forms would have the formulæ



The instability of the partially substituted ammonium hydroxides is explained by assuming that owing to the presence of labile hydrogen the transformation into the hydronium form always occurs, and hence these bases have the characters of ammonium hydroxide itself. In the case of the tetra-alkyl ammonium hydroxides, this change is excluded, and, accordingly, these compounds are carbonium bases, differing from ammonium hydroxide in stability and in electrochemical behaviour.

According to this theory, two isomeric forms of the compound  $(\text{NBA}_3)\text{X}$ , are possible, and isomerism of this order has been observed by Le Bel, Schryver, and Aschan, Le Bel's isomeric salts being thus represented:  $\text{X}\cdot\text{H}_2\text{CPr}\cdots\text{NMe}_3$ , and  $\text{X}\cdot\text{H}_3\text{C}\cdots\text{NMe}_3\text{C}_4\text{H}_9$ .

These hypotheses are also applied to the constitution of the unsatur-



ated cyclic bases and to the diazonium salts ; the discussion is, however, of such a nature that it cannot be profitably abstracted. G. T. M.

**New Extraction Apparatus.** By O. STEPHANI and TH. BÖCKER (*Ber.*, 1902, **35**, 2698—2700).—The apparatus described is suitable for the extraction of liquids with a denser solvent, or for the extraction of solids with any solvent. It was found to work very well in such cases as the extraction of strong alkaline or acid solutions with chloroform, otherwise difficult owing to the formation of emulsions or the precipitation of inorganic salts. R. H. P.

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## Inorganic Chemistry.

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**Chlorinating Action of a Mixture of Hydrochloric Acid and Oxygen.** By CAMILLE MATIGNON (*Compt. rend.*, 1902, 134, 1497—1499).—Spongy platinum placed in a concentrated solution of hydrochloric acid in contact with the air is acted on, chloroplatinic acid being formed. There is no action on platinum foil at the ordinary temperature, but when this is heated at  $170^{\circ}$  for 5 hours with hydrochloric acid in a sealed tube containing oxygen, the platinum is dissolved. Gold foil is attacked under the same conditions at  $180^{\circ}$ ; amorphous gold is not acted on in the cold. Tellurium is readily dissolved by the combined action of hydrochloric acid and oxygen.

J. MCC.

**Stability of Hypochlorites and Hypobromites.** By CARL GRAEBE (*Ber.*, 1902, 35, 2753—2756).—Hypochlorite solutions are much more readily prepared than hypobromite, as unless the bromine is added very slowly, considerable amounts of bromate are formed. One of the simplest methods of generating chlorine is from permanganate and hydrochloric acid; the increase in weight of the alkaline solution gives the amount of chlorine absorbed; in all cases, however, this amount is practically the theoretical quantity which could be obtained from the permanganate employed. A 10 per cent. solution of the alkali hydroxide is employed, and the resulting hypochlorite solution contains 5.5 grams of available chlorine per 100 c.c., and may be kept for some time in the dark without undergoing deterioration if excess of alkalis is present.

Hypobromite solutions are much less stable even when excess of alkali is present.

J. J. S.

**Preparation of Periodic Acid by Electrolysis.** By ERICH MÜLLER and O. FRIEDBERGER (*Ber.*, 1902, 35, 2652—2659. Compare Abstr., 1901, ii, 380).—On more closely investigating the formation of periodate in the electrolysis of an alkaline solution of iodate, it was found that the difference of potential between the electrodes became

greater during the electrolysis, and that, at the same time, the current efficiency in yield of periodate very largely increased. The accumulation of oxygen on the anode during electrolysis was the cause of this change. When lead peroxide was used as anode, iodic acid, which is not oxidised when platinum electrodes are employed, could be completely oxidised to periodic acid. In a small, porous cell containing 50 per cent. iodic acid, the anode, consisting of a U-shaped lead tube coated with peroxide, was placed; the cathode was platinum foil immersed in 2*N* sulphuric acid; the anode was cooled by running water through the lead tube. At a temperature of 12–13°, and using a current density of 0.28 ampere per sq. cm. at the anode, the whole of the iodic acid was converted into periodic acid, a slight loss occurring through diffusion. Replacement of the lead peroxide by manganese peroxide caused only a trace of iodic acid to be oxidised. When a solution of iodic acid is allowed to remain in contact with lead peroxide for a long time, a small quantity of periodic acid is formed. To isolate the acid from the anode liquid, the solution after dilution and filtration was evaporated, when periodic acid was obtained pure in large crystals.

In order to estimate periodic acid in the presence of iodic acid, the solution is exactly neutralised, using phenolphthalein as indicator; excess of potassium hydrogen carbonate is then added and potassium iodide; the periodate is reduced to iodate, and the equivalent amount of iodine which is set free is titrated with standard arsenious acid; this gives a quarter of the oxygen present as periodate; the total oxygen present, both as periodate and as iodate, is estimated by titrating the iodine set free from the acidified mixture.

K. J. P. O.

**Hydrides of the Second [Sulphur] Family of Metalloids.** By ROBERT DE FORCRAND and HENRI FONZES-DIACON (*Ann. Chim. Phys.*, 1902, [vii], 26, 247–271. Compare Abstr., 1900, ii, 405).—A detailed account of the study of the carefully purified hydrides of sulphur, selenium, and tellurium obtained by the decomposition of the corresponding aluminium compounds by water or dilute acid. Hydrogen selenide has the most toxic effect, the physiological action of the telluride being comparatively slight. A comparison of the physical properties of these gases with those of water affords a striking illustration of the rule that, in a given family of elements, and particularly in the oxygen and fluorine groups, the first and fourth terms differ markedly from their neighbours, whilst the two median elements resemble each other very closely.

G. T. M.

**Fluorides and Oxyfluorides of Sulphur.** By HENRI MOISSAN and PIERRE LEBEAU (*Ann. Chim. Phys.*, 1902, [vii], 26, 145–178).—A detailed account of work already published (compare Abstr., 1900, ii, 341, 342, 472; 1901, ii, 233). The results obtained indicate that fluorine, although the initial member of the halogen family, does not closely resemble chlorine and bromine. Sulphuryl fluoride and thionyl fluoride are far more inert than the corresponding chlorine derivatives, and sulphur hexafluoride is an unexpectedly stable substance. In certain respects, fluorine seems to behave like oxygen.

G. T. M.

**Persulphuric Acids.** By HENRY E. ARMSTRONG and T. MARTIN LOWRY (*Proc. Roy. Soc.*, 1902, **70**, 94—99).—When Caro's acid is neutralised and the resulting solution heated, it becomes acid; it may further be shown that the ratio of increase in acidity to active oxygen lost ( $\text{SO}_3 : \text{O}$ ) is 1 : 2. This result is not in harmony with the formula,  $\text{H}_2\text{S}_2\text{O}_8$ , assumed by Baeyer and Villiger (*Abstr.*, 1901, ii, 380), for the salts of this acid would remain neutral after the removal of peroxide oxygen, thus:  $2\text{CaSO}_5 = 2\text{CaSO}_4 + \text{O}_2$ . On the other hand, the facts would be explained by the assumption of the formula  $\text{H}_2\text{S}_2\text{O}_9$ , for  $\text{CaS}_2\text{O}_9 + \text{H}_2\text{O} = \text{CaSO}_4 + \text{H}_2\text{SO}_4 + \text{O}_2$ . The acid  $\text{H}_2\text{S}_2\text{O}_9$  may be regarded as the anhydro-acid derived from permonosulphuric acid, that is, as  $\text{O}(\text{SO}_2 \cdot \text{O} \cdot \text{OH})_2$ . Reviewing the results obtained by Baeyer and Villiger (*loc. cit.*) and those by Lowry and West (*Trans.*, 1900, **77**, 950), the authors think it necessary to assume that there are at least three persulphuric acids:

1. Pertetrasulphuric acid,  $\text{O}_2(\text{SO}_2 \cdot \text{O} \cdot \text{SO}_2 \cdot \text{OH})_2$ .
2. Perdisulphuric acid,  $\text{O}_2(\text{SO}_2 \cdot \text{OH})_2$ .
3. Peranhydrosulphuric acid (Caro's acid).

J. C. P.

**Compounds of Tellurium with Bismuth and the Quantitative Separation of the Two Elements.** By ALEXANDER GUTBIER (*Zeit. anorg. Chem.*, 1902, **31**, 331—339. Compare *Abstr.*, 1901, ii, 687).—Tellurium and bismuth alloy in all proportions. The alloys were prepared by fusing a mixture of the finely-divided metals in a current of hydrogen. When tellurium is in excess, the alloy is grey, brittle, and when broken shows a silvery lustre; when bismuth is in excess, the alloy has a high metallic lustre and is not so brittle.

These elements can best be separated by shaking the precipitated sulphides with a solution of potassium sulphide. The tellurium in the solution can be precipitated by hydrazine hydrochloride or by sulphurous acid. When sulphurous acid is employed, the sulphuric acid formed can be removed by means of a solution of barium hydrogen carbonate.

J. McC.

**Some Salts of Telluric Acid.** By ALEXANDER GUTBIER (*Zeit. anorg. Chem.*, 1902, **31**, 340—351).—The potassium tellurate,  $\text{K}_2\text{TeO}_4 \cdot 5\text{H}_2\text{O}$ , is obtained from a solution of telluric acid and one of potassium hydroxide. It separates in long, colourless needles which are very easily soluble in water. When heated to  $300^\circ$ , it loses oxygen and gives potassium tellurite. The salt,  $\text{K}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ , is obtained when telluric acid is dissolved in a concentrated boiling solution of potassium hydroxide, and the corresponding sodium salt is obtained in the same way. This sodium salt can also be obtained by adding absolute alcohol to a well-cooled solution of telluric acid and sodium hydroxide. It also gives off oxygen when heated. The sodium salt is much less soluble than the potassium salt.

The following tellurates can be obtained from a solution of the potassium salt; ceric tellurate as a pasty mass; thorium tellurate as a white, curdy precipitate; uranyl tellurate as a yellow, curdy precipitate; and zinc tellurate as a white precipitate.

With a neutral solution of silver nitrate, a solution of potassium

tellurate gives silver tellurate as a dark yellow precipitate which decomposes very easily into a basic tellurate.

It has not been possible to prepare any esters of telluric acid.

J. McC.

**Electrolytic Reduction of Nitric Acid in Presence of Hydrochloric Acid or Sulphuric Acid.** By JULIUS TAFEL (*Zeit. anorg. Chem.*, 1902, 31, 289—325).—When nitric acid is electrolysed, it suffers reduction, and in order to diminish the action of the nitric acid as an electrolyte a relatively large amount of sulphuric acid or hydrochloric acid was added to the solution. The product of the reduction is largely dependent on the nature of the metal used as electrode. With platinum, no appreciable reduction takes place, and with palladium the reduction is extremely slow. The chief products of the reduction are hydroxylamine and ammonia. The largest proportion of hydroxylamine is formed when mercury is used as the electrode, and the conversion of the nitric acid into this can be carried out almost quantitatively. With lead electrodes, about 40 per cent. of the nitric acid is converted into hydroxylamine, and with copper electrodes only about 15 per cent.; if the copper be in the form of a spongy mass, only about 1 per cent. of the acid is transformed into hydroxylamine, the remainder being reduced to ammonia. When an amalgamated electrode is used, the reduction takes place in the same way as when a mercury electrode is employed.

Hydroxylamine is not altered when subjected to electrolysis between copper electrodes. It is thus proved that the reduction of the nitric acid takes place in two ways independent of each other, the one giving hydroxylamine, the other ammonia; the course of the reaction depends on the specific nature of the electrode.

The current yield and the proportion of hydroxylamine formed when the nitric acid is electrolysed between electrodes of lead, cadmium, copper, silver, aluminium, tin, bismuth, nickel, and carbon are given in tables. The amount of hydroxylamine produced is greater as the solution of nitric acid is more dilute; in order to obtain the largest proportion, a very dilute solution of nitric acid should be employed, and more added as the reduction proceeds. When the amount of sulphuric acid present falls below 40 per cent., the quantity of hydroxylamine formed decreases appreciably, but otherwise the concentration of the sulphuric acid exerts no influence on the reaction.

In some experiments, the amounts of ammonia and of nitrogenous gas evolved, as well as the hydroxylamine, were determined. The amount of gas was always small.

The action of copper, mercury, and lead on nitric acid in presence of sulphuric acid has also been studied. With copper or mercury, no hydroxylamine is produced, and with lead reduction to nitrous acid takes place.

In the production of hydroxylamine, the current yield is greatest for lead, slightly smaller for amalgamated lead, and decidedly less for copper. The presence of nitrous acid exerts no appreciable influence on the reduction of nitric acid by these metals.

Incidentally, it has been proved that hydroxylamine sulphate is very

stable in presence of sulphuric acid, and the solution may be warmed to about  $40^{\circ}$  without any decomposition occurring.

The author believes that the electrolytic reduction of nitric acid may prove the best method of preparing hydroxylamine provided that suitable electrodes are used, that the temperature is kept low, that the nitric acid is employed in sufficiently dilute solution, and that fairly concentrated sulphuric acid is added to the solution.

Hydroxylamine hydrochloride can also be conveniently obtained when hydrochloric acid is employed in place of sulphuric acid, but the process is unpleasant on account of the simultaneous evolution of chlorine. J. McC.

**The Mixtures formed by Sulphur and Phosphorus below  $100^{\circ}$ .** By R. BOULOUCH (*Compt. rend.*, 1902, 135, 165—168).—The curve of solidification for varying proportions of sulphur and phosphorus has been determined. This consists of two lines which cut sharply at a point representing  $9.8^{\circ}$  and 22.8 per cent. of sulphur in the mixture. This is an eutectic point. The author concludes that below  $100^{\circ}$  no definite compound of sulphur and phosphorus is formed. Mixed crystals of sulphur and phosphorus, rich in sulphur, can be formed, and these are isomorphous with octahedral sulphur. Mixed crystals rich in phosphorus can also be isolated at low temperatures and these are isomorphous with phosphorus. J. McC.

**New Properties of Amorphous Silicon.** By HENRI MOISSAN and SAMUEL SMILES (*Compt. rend.*, 1902, 134, 1552—1553).—The amorphous silicon, obtained by sparking liquid silicon hydride (see following abstract), forms long filaments and possesses remarkable reducing properties. Thus neutral potassium permanganate is reduced slowly in the cold, copper sulphate and gold chloride on boiling; mercuric chloride is reduced to calomel. In these properties, silicon resembles pure boron (*Abstr.*, 1892, 1153). K. J. P. O.

**New Researches on Liquid Silicon Hydride.** By HENRI MOISSAN and SAMUEL SMILES (*Compt. rend.*, 1902, 134, 1549—1552. Compare this vol., ii, 318).—The vapour density of liquid silicon hydride, taken by Gay-Lussac's method at  $100^{\circ}$ , was 2.37, corresponding with that required for the formula  $\text{Si}_2\text{H}_6$ .

On sparking the vapour under reduced pressure for 15 minutes, it is completely decomposed into amorphous silicon and hydrogen. The hydride is soluble in ethyl silicate and slightly so in water; in the latter solution, it is gradually oxidised. It reduces aqueous ferric chloride, forming a brown precipitate insoluble in hydrochloric acid; a dilute solution of indigo is decomposed with the production of a green precipitate; both acidified potassium dichromate and neutral permanganate are immediately reduced. When the gas is bubbled through warm bromine water, each bubble becomes coated with a layer of silica; nitric acid produces a similar effect; concentrated hydrochloric acid is without action; sulphuric acid dries the gas and causes it to explode more violently when brought in contact with air. On mixing the substance with carbon tetrachloride, a violent explosion with the

production of a flame occurs, hydrogen chloride, carbon, and silicon being formed; it also explodes violently with sulphur hexafluoride.

K. J. P. O.

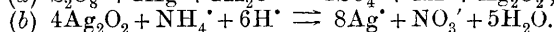
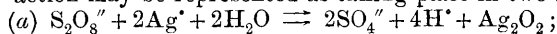
**Cæsium Compounds.** By CAMILLE CHABRIÉ (*Ann. Chim. Phys.*, 1902, [vii], 26, 212—228. Compare Abstr., 1901, ii, 314, 600).—*Cæsium vanadate*,  $\text{CsVO}_3$ , is a crystalline salt obtained by boiling vanadic anhydride with a solution of cæsium carbonate. The other compounds of cæsium referred to in this communication have already been described.

G. T. M.

**Crystallography of Ammonium Haloid Compounds.** By FR. SLAVÍK (*Zeit. Kryst. Min.*, 1902, 36, 268—276).—Crystallographic determinations are given for ammonium chloride, ammonium bromide, and ammonium iodide, and for tetramethylammonium iodide, tetraethylammonium iodide, and tetrapropylammonium iodide. Although these belong to different crystal-systems, yet a certain relation is traced between the topic axes.

L. J. S.

**Action of Silver Salts on Solutions of Ammonium Persulphate.** By HUGH MARSHALL and J. K. H. INGLIS (*Proc. Roy. Soc. Edin.*, 1902, 24, 88—93).—It has previously been shown (*Proc. Roy. Soc. Edin.*, 23, 163) that, in presence of a soluble silver salt, ammonium persulphate is decomposed with formation of nitric and sulphuric acids. On the assumption that silver peroxide is formed immediately, the action may be represented as taking place in two stages:



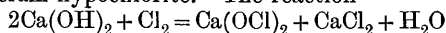
The total silver concentration being small compared with the persulphate concentration, the concentration of  $\text{Ag}^*$  and  $\text{Ag}_2\text{O}_2$  may be regarded as constant; equation (a) is then unimolecular, and in fact the course of the reaction, as indicated by the increase of acidity, corresponds with that required by the equation  $dc/dt = KC$ , where  $C$  is the concentration of the persulphate ions. When sodium nitrate, ammonium sulphate, or ammonium nitrate is added to the reaction mixture,  $K$  is still constant, but has a rather smaller value than when no neutral salt has been added, the neutral salt diminishing the concentration of the persulphate ions. When nitric or sulphuric acid is added to the reaction mixture, the reaction appears at first to be accelerated, but the end point is not the same as in the previous cases, probably owing to some other action that produces less acid, such as  $2\text{Ag}_2\text{O}_2 + 4\text{H}^* = 4\text{Ag}^* + \text{O}_2 + 2\text{H}_2\text{O}$ . Instead of assuming that  $\text{Ag}_2\text{O}_2$  is formed, it may be assumed that silver peroxide is a very feebly basic oxide the salts of which are readily hydrolysed.

J. C. P.

**Silver-chabazite and Silver-analcite.** By GEORGE STEIGER (*Amer. J. Sci.*, 1902, [iv], 14, 31—32).—Analcite, or the artificial product ammonium-analcite (this vol., ii, 269), when fused for some time with silver nitrate yields a product with the composition  $\text{Ag}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2, 2\text{H}_2\text{O}$ , this being the analcite formula with silver in place of sodium. The ammonium derivative of chabazite is acted on by silver nitrate in the same way.

L. J. S.

**Composition of Bleaching Powder.** By WOLDEMAR VON TIESENHOLT (*J. pr. Chem.*, 1902, [ii], 65, 512—527. Compare Abstr., 1901, ii, 154).—Contrary to Foerster's assumption (Abstr., 1899, ii, 278), the evolution of chlorine brought about by mixing aqueous solutions of sodium chloride and hypochlorous acid is not due to formation of chloric acid, but must take place according to the equation  $\text{NaCl} + \text{HClO} = \text{NaOH} + \text{Cl}_2$ . The presence of calcium hypochlorite in bleaching powder is shown by extracting with alcoholic chloroform; the residue contains the percentage of chlorine as calcium chloride unchanged, the chloroform solution on titration with sodium thio-sulphate gives results approximately equivalent to the calculated amount of calcium hypochlorite. The reaction



is reversible. The evolution of chlorine, when bleaching powder is heated, is demonstrated by boiling with carbon tetrachloride, which dissolves chlorine but not hypochlorous acid. Chlorine is also evolved when bleaching powder is ground with calcium chloride.

G. Y.

**The Atomic Weight of Radium.** By SKŁODOWSKA CURIE (*Compt. rend.*, 1902, 135, 161—163).—The atomic weight of radium was determined by estimating the quantity of chlorine in radium chloride which was obtained by fractional crystallisation of radiferous barium chloride. The mean value of the results found is 225 and the author thinks that this is correct to 1 unit. Anhydrous radium chloride is spontaneously luminous. In chemical properties, radium is an element of the alkaline earth series.

J. McC.

**Precipitation of Cupric Chloride and Bromide by Sulphuric Acid.** By GEORGES VIARD (*Compt. rend.*, 1902, 135, 168—170).—By the addition of excess of concentrated sulphuric acid to a solution of cupric chloride, the yellowish, anhydrous salt is deposited if there is more than 68 per cent. of sulphuric acid present. If the acid be added slowly so that the temperature does not rise too high, the chloride is scarcely decomposed and the precipitation is almost complete. If the quantity of sulphuric acid added is too small, the green dihydrate,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , is deposited.

The action with cupric bromide is quite analogous; the black, anhydrous salt can be completely precipitated. The bromide is, however, attacked by the sulphuric acid to a slightly greater extent than the chloride; although, even at a high temperature, the decomposition is very small. These reactions may be used to differentiate between a chloride and a bromide.

J. McC.

**Yellow Cuprous Oxide.** By MAX GRÖGER (*Zeit. anorg. Chem.*, 1902, 31, 326—330).—It has not been possible to obtain cuprous oxide quite pure by precipitating a solution of cuprous chloride with sodium hydroxide. If, however, a clear solution of cuprous chloride is slowly dropped into a concentrated solution of sodium chloride in excess of sodium hydroxide (also containing some potassium hydrogen tartrate) which is violently stirred, the cuprous oxide is obtained as a



yellow precipitate which is washed with a solution of sodium chloride, then with pure water. When dried, it forms a brownish-yellow powder. It contains no combined water, and is therefore not a hydroxide. It appears to be a hydrated, amorphous, cuprous oxide.

J. McC.

**Cerium Silicide.** By JEAN STERBA (*Compt. rend.*, 1902, 135, 170—172).—By heating together cerium oxide and silicon in the electric furnace, cerium silicide,  $\text{CeSi}_2$ , is formed. It forms small crystals with a steely lustre which give a black powder; the density at  $17^\circ$  is 5.67. It is only slowly acted on by water; hydrogen is without action on it. Fluorine acts in the cold on it, chlorine, bromine, or iodine only after heating. When heated to redness, it burns in oxygen with a vivid incandescence and when heated in boiling sulphur or selenium, it burns. Hydrogen chloride acts on it at a red heat. Solutions of hydrochloric and hydrofluoric acids attack it with evolution of hydrogen. Hydrogen sulphide and water are attacked at a red heat. Alkalis and ammonia do not react with it in the cold.

J. McC.

**Redetermination of the Atomic Weight of Lanthanum.** By HARRY C. JONES (*Amer. Chem. J.*, 28, 1902, 23—34).—The double nitrate of ammonium and lanthanum was fractionally crystallised until spectroscopic examination showed that it contained no impurity except a trace of cerium. It was then ignited, and the resulting oxide was dissolved in dilute nitric acid. The nitrate solution was treated with specially purified oxalic acid; the oxalate was ignited, the oxide was redissolved in nitric acid, and the oxalate reprecipitated and again ignited. When the product was heated to redness in a current of hydrogen, its weight remained constant, showing that no higher oxide than the sesquioxide was present. A weighed quantity of this oxide was then converted into the sulphate. Brauner and Pavlíček (*Trans.*, 1901, 81, 1243) have expressed the opinion that the sulphate method is untrustworthy, owing to the presence of the acid sulphate in the product; the author, however, was able to obtain the salt free from the acid sulphate and found that the presence or absence of the latter depends on the temperature to which the sulphate has been heated. The mean of 12 determinations gave the atomic weight 138.77 ( $\text{O} = 16$ ,  $\text{S} = 32.06$ ).

An attempt was made to determine the atomic weight by means of the oxalate, but the method was abandoned on account of the impossibility of obtaining the oxalate of constant weight.

E. G.

**Action of Hydrochloric Acid on the Sulphates of Aluminium, Chromium, and Iron.** By ALBERT RECOURA (*Compt. rend.*, 1902, 135, 163—165).—By the action of hydrochloric acid on aluminium sulphate and chromium sulphate, the chlorosulphates,  $\text{AlSO}_4\text{Cl} \cdot 6\text{H}_2\text{O}$  and  $\text{CrSO}_4\text{Cl} \cdot 6\text{H}_2\text{O}$ , have been obtained.

The chromium chlorosulphate was prepared by dissolving chromium sulphate in hot concentrated hydrochloric acid. On cooling, it separates as a green powder which is very soluble in water. Cryoscopic experiments show that the salt has the simple formula given. The chlorine which it contains is not precipitable by silver nitrate, but the sulphuric acid is completely precipitated by barium chloride.

When kept at  $85^{\circ}$ , it gradually loses water; when 1 mol. has been lost and the residue,  $\text{CrSO}_4\text{Cl}\cdot 5\text{H}_2\text{O}$ , is dissolved in water, the solution gives no precipitate with barium chloride. The molecular lowering of the freezing point of water brought about by this salt is 18.8, proving that it does not undergo dissociation.

No corresponding ferric chlorosulphate has been obtained.

J. McC.

**Action of Fused Sodium Dioxide on Metals.** By WILLIAM L. DUDLEY (*Amer. Chem. J.*, 1902, 28, 59—66. Compare Abstr., 1897, ii, 171).—When nickelo-nickelic hydroxide is heated at  $240^{\circ}$ , nickelo-nickelic oxide,  $\text{Ni}_3\text{O}_4$ , is obtained as a hygroscopic, black, amorphous powder which absorbs 7.4 per cent. of water from the air at  $30^{\circ}$ , but loses it completely at  $110^{\circ}$ ; it is non-magnetic, and differs markedly from the oxide prepared by Baubigny (Abstr., 1879, 299) by passing oxygen over heated nickel chloride.

Iron, gold, silver, and platinum are rapidly attacked by fused sodium dioxide. In the case of iron, dark-red, tabular crystals are produced which have the composition  $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ , and sp. gr. 3.8 at  $27^{\circ}$ . This substance is magnetic, and when heated to low redness leaves a residue of the oxide,  $\text{Fe}_2\text{O}_3$ , which is also magnetic.

When sodium dioxide is fused on gold, oxidation seems to take place, but the oxide formed is immediately decomposed, leaving the metal in a spongy state.

In the case of silver, the fused mass becomes filled with needle-shaped crystals; if the product is washed in a Soxhlet extraction apparatus, a black, amorphous residue is obtained and the washings gradually become wine-coloured. Both the precipitate and washings are found to contain silica, the presence of which is due to corrosion of the glass apparatus. By washing the product of the fusion in a platinum Gooch crucible, grey crystals were obtained of the composition Ag, 97.99; O, 1.82 per cent.; after washing this substance with strong ammonia, the residue was found to contain only 0.175 per cent. of oxygen.

When spongy platinum is heated with fused sodium dioxide, and the product washed with water, a yellowish substance is obtained which seems to consist of an unstable sodium salt of the yellow hydroxide. After neutralising the alkali and again washing, the product has the composition  $\text{Pt}_2\text{O}_3\cdot 2\text{H}_2\text{O}$ ; it is reduced to platinum black by boiling with sodium hydroxide and alcohol. It is insoluble in nitric and sulphuric acids and in cold dilute hydrochloric acid, but is dissolved by hot concentrated hydrochloric acid in presence of air with formation of platinic chloride. It does not lose water at  $100^{\circ}$ , but loses 5.22 per cent. at  $385^{\circ}$ , and at about  $450^{\circ}$  is converted into platinum sesquioxide,  $\text{Pt}_2\text{O}_3$ , which forms a dark-brown, amorphous powder.

E. G.

**Chromium Hydroxide.** By W. FISCHER and W. HERZ (*Zeit. anorg. Chem.*, 1902, 31, 352—358).—Freshly precipitated chromium hydroxide is soluble in solutions of alkalis, but is easily converted (by drying or heating) into a modification which is insoluble. From

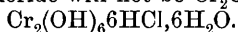
dialysis experiments with the solution in alkali, it is evident that the chromium hydroxide is dissolved in the colloidal form, and this is confirmed by the results obtained for the conductivity of the alkali solution before and after having the chromium hydroxide dissolved in it.

Ammonia dissolves chromium hydroxide forming a reddish-violet solution, from which the hydroxide, however, separates on standing. Methylamine behaves like ammonia, whilst dimethylamine and trimethylamine at once precipitate the chromium hydroxide completely. Tetramethylammonium hydroxide behaves like potassium or sodium hydroxide.

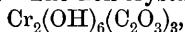
J. McC.

**Constitution of the Compounds of Chromium. I.** By GRÉGOIRE N. WYROUBOFF (*Bull. Soc. Chim.*, 1902, [iii] 27, 666—679).—If potassium oxalate is added to a solution of any violet salt of chromium, prepared in the cold, violet crystals of chromium oxalate,  $\text{Cr}_2\text{O}_3 \cdot 3\text{C}_2\text{O}_3 \cdot 25\text{H}_2\text{O}$  are obtained, which on being left exposed to the air, pass into a lower hydrate containing  $12\text{H}_2\text{O}$ . If the latter, placed in a well-corked tube, be heated to more than  $25^\circ$ , it liquefies to a liquid of the same composition. Dried over sulphuric acid, a violet "varnish" containing  $7\text{H}_2\text{O}$  is obtained, and on heating to  $110^\circ$  there is a loss of  $3\text{H}_2\text{O}$ , the colour at the same time becoming green.

To explain the various facts concerning the different compounds of chromium, the author considers the existing ideas with regard to salt formation to be too simple. With reference to the sesquioxides in particular, he considers that their compounds contain water of constitution when they form *normal* salts and become anhydrous only when they become 'complex compounds'; they act, not only in virtue of the metal, but also and especially in virtue of the hydroxyl groups which they contain. In the interaction with acids, the latter act as points of attachment for the acid. Applying these views, the formula of crystalline chromium chloride will not be  $\text{Cr}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ , but



If any of the hydroxyl groups take part in the interaction, not *salts*, but *esters*, will be obtained. The non-crystallisable oxalate,



the author regards, not as a salt, but as a true ester. He also arrives at the conclusion that the hydroxide of the green compounds is not  $\text{Cr}_2(\text{OH})_6$ , in which the hydroxyl groups have all the same function, but an hydroxide,  $\text{Cr}_2(\text{OH})_2(\text{OH})_4$ , in which the hydroxyl groups are partly acid and partly basic. So long as there are six hydroxyl groups to form  $\text{Cr}_2(\text{OH})_6$ , the compounds will be violet; if water is withdrawn, the hydroxyl groups become individualised and the compounds are green. For sulphochromic acid, the author proposes the formula  $\text{Cr}_2\text{O}_2(\text{OH})_2(\text{OH})_2(\text{SO}_2)_4\text{O}_2(\text{OH})_2$ .

A. F.

**Action of Hydrogen Peroxide and Sodium Hypochlorite on the Oxides of Thorium, Zirconium, and Cerium.** By L. PISSARJEWSKY (*Zeit. anorg. Chem.*, 1902, 31, 359—367).—By the action of hydrogen peroxide on a concentrated solution of thorium nitrate, a precipitate is formed which is probably thorium peroxide,  $\text{Th}(\text{O}_2\text{H})_4$ . This suffers hydrolysis, so that  $\text{Th}(\text{O}_2\text{H})_3 \cdot \text{OH}$  and  $\text{Th}(\text{O}_2\text{H})_2(\text{OH})_2$  are pro-

duced on washing the precipitate. With zirconium, a similar result is obtained. With ceric sulphate, a gelatinous substance is formed which resembles ceric peroxide, and at the same time a pulverulent precipitate is produced which may be a compound of the peroxide,  $\text{CeO}_3$ , with sulphuric acid.

The peroxides of the three metals can be obtained by treatment of the hydroxides with hydrogen peroxide. The following heats of neutralisation of 1 mol. of the hydroxide and 1 mol. of hydrogen peroxide have been calculated:  $\text{Th}(\text{OH})_4$ , 8.810 cal.;  $\text{Ce}(\text{OH})_4$ , 2.704 cal.; and  $\text{Zr}(\text{OH})_4$ , 1.314 cal.

The action of hypochlorite on solutions of thorium salts was studied by examining the products of the electrolysis of a mixed solution of an alkaline solution of sodium chloride and thoric oxide. At the same temperature and with the same current strength, the proportion of  $\text{ThO}_2$  which passes into the peroxide,  $\text{ThO}_3$ , is independent of the total amount of thorium present. The proportion of peroxides formed increases with the temperature and with the current strength.

By the electrolytic process, the existence of  $\text{CeO}_3$  could not be proved.  
J. McC.

**Metathorium Oxychloride.** By HENRY P. STEVENS (*Zeit. anorg. Chem.*, 1902, 31, 368—372).—The author maintains the conclusions previously given (Abstr., 1901, ii, 391) as to the composition and nature of metathorium oxychloride against the criticism of Wyruboff (Abstr., 1901, ii, 604).

The method of preparing the oxychloride by means of the oxalate is better than that adopted by Wyruboff. The opalescence of the solution is due to the oxychloride and not to any impurity, as Wyruboff suggests.  
J. McC.

**Double Nitrites of Iridium.** By ÉMILE LEIDIE (*Compt. rend.*, 1902, 134, 1582—1584. Compare Abstr., 1901, ii, 62).—When aqueous potassium nitrite is added to a concentrated solution of potassium irido- or iridi-chloride, a yellow or rose-coloured precipitate is obtained, which consists of a mixture of a double nitrite of potassium and iridium and potassium chloride, and is not a compound of the double nitrite and potassium iridochloride, as Lang thought; it yields only a trace of hydrogen chloride when heated with hydrogen, and dissolves in boiling water, but deposits, on cooling, a solid still containing some potassium chloride, from which it cannot be freed by this process.

A double *chloronitrite*,  $\text{Ir}_2\text{Cl}_2(\text{NO}_2)_4 \cdot 6\text{KCl}$ , is prepared by mixing solutions of potassium nitrite and iridochloride, filtering off the precipitate, saturating with potassium chloride, and evaporating at a low temperature; the salt forms lemon-yellow crystals and is decomposed by boiling water; it is identical with the salt described by Gibbs as the double nitrite.

The double *nitrite*,  $\text{K}_6\text{Ir}_2(\text{NO}_2)_{12}$ , is obtained by adding potassium nitrite to a warm solution of iridium sulphate; it is a white powder, insoluble in cold water, and is converted by hydrochloric acid into the iridichloride. The corresponding sodium salt is soluble and can be pre-

pared in a similar manner. The *ammonium* salt,  $(\text{NH}_4)_6\text{Ir}_2(\text{NO}_2)_{12}$ , is prepared from the sodium salt, and is nearly insoluble in cold water ; when boiled with water, nitrogen is evolved.

K. J. P. O.

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## Mineralogical Chemistry.

**Italian Petroleum.** By LUIGI BALBIANO (*Gazzetta*, 1902, 32, i, 437—447).—[With MARIO PALLADINI.]—Examination of a sample of petroleum from Valleia, near Piacenza, shows that the fractions distilling at 57—87° contain no olefines, but probably methylcyclopentane, cyclohexane and benzene.

T. H. P.

**Roumanite from the Black Sea.** By CONSTANTIN I. ISTRATI (*Bull. Soc. Sci. Bucarest*, 1901, 9, 650—652).—A small piece of yellow, translucent amber has been found in the sand on the coast of the Black Sea at Tékir-Ghiol. It differs somewhat in composition from other specimens of Roumanian amber (compare Abstr., 1897, ii, 502; 1898, ii, 523):

C.	H.	S.	Ash.	Sp. gr.
79·74	10·15	2·53	0·043	1·0985

L. J. S.

**Greenockite on Calcite from Joplin, Missouri.** By H. B. CORNWALL (*Amer. J. Sci.*, 1902, [iv], 14, 7—8).—The bright yellow, dusty coating on calcite from Joplin, Missouri, was found to contain about 30 per cent. of cadmium sulphide; it is therefore mainly greenockite (CdS), like the yellow coating on zinc-blende from the same locality.

L. J. S.

**Manganiferous Nodules in the Boulder-clay of Essex.** By MAY THRESH (*Essex Naturalist*, 1902, 12, 137—139. Compare Abstr., 1898, ii, 390).—In certain soils in Essex, where these overlie boulder-clay, there are present, to the extent of 0·1 per cent., small, hard, black nodules resembling seeds in appearance, the largest being 5 mm. in diameter. The following analyses of these nodules show that they consist of siliceous sand cemented by iron and manganese oxides, with some calcium phosphate and carbonate:

SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MnO <sub>2</sub> .	MnO.	CaO.	H <sub>2</sub> O. P <sub>2</sub> O <sub>5</sub> , CO <sub>2</sub> , &c.	Total.
47·90	29·91	5·12	3·44	2·45	7·00	100·00
51·86	23·89	9·35	2·07	3·54	5·60	100·00

The manganese oxides have probably been deposited from an alkaline solution.

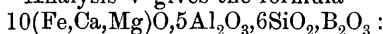
L. J. S.

**Crystalline Limestones of Ceylon.** By ANANDA K. COOMÁRA-SWÁMY (*Q. J. Geol. Soc.*, 1902, 58, 399—422. Compare Abstr., 1901, ii, 110).—A description is given of the crystalline limestones and

their mode of occurrence, especially in the Kandy and Hakgala districts. The limestones enclose several silicates (forsterite, phlogopite, diopside, amphibole, clinohumite, scapolite) and other accessory minerals (spinel, blue apatite, pyrite, graphite). The following mineral analyses (I and V by G. T. Prior; II—IV by W. C. Hancock) are given. I, Forsterite from Hakgala; II, forsterite from Ampitiya; III, colourless amphibole; IV, clinohumite from Gettembe;

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	Na <sub>2</sub> O.	H <sub>2</sub> O.	F.	Total.	Sp. gr.
I.	42·55	0·23	—	2·36	1·43	51·97	—	1·68	—	100·22	3·14
II.	41·16	—	2·58	—	—	52·60	—	3·8	—	100·14	3·13
III.	47·04	13·76	trace	—	13·39	21·26	4·01	0·60	—	100·36	2·92
IV.	37·52	trace	9·00	—	—	49·75	1·44	1·50	1·02	100·23	—

A new mineral, *serendibite*, was found in diopside-bands between limestone and acid granulite in the moonstone pits at Gangapitiya, twelve miles east of Kandy. The embedded crystals are of a dark bluish-green colour and are strongly pleochroic (very pale yellowish-green to deep indigo-blue). The optical characters and repeated twinning indicate that the mineral is probably triclinic. Sp. gr. 3·42; hardness about 7. Analysis V gives the formula



SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O, Li <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .	Loss on igni- tion.	F.	B <sub>2</sub> O <sub>3</sub> .	Total.
V. 25·33	34·96	4·17	14·56	14·91	0·22	0·51	0·48	0·69	trace	[4·17]	100·00

L. J. S.

**Occurrence of Uranophane in Georgia.** By THOMAS L. WATSON (*Amer. J. Sci.*, 1902, [iv], 13, 464—466).—Uranophane has been found at Stone Mountain, 16 miles east of Atlanta, as a thin, sulphur-yellow to lemon-yellow incrustation on the surfaces of joint planes in granite. Deducting impurities (MgO 1·98, Al<sub>2</sub>O<sub>3</sub> 6·33 per cent., Fe<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>), the recalculated analysis is given as :

CaO.	UO <sub>3</sub> .	SiO <sub>2</sub> .	H <sub>2</sub> O.	Total.
6·14	61·37	18·93	13·56	100·00

This corresponds with the formula CaO, 2UO<sub>3</sub>, 3SiO<sub>2</sub>, 7H<sub>2</sub>O. The excess of silica over that given in Genth's formula, is probably due to the presence of hyalite, which is deposited on the uranophane.

The grey, biotite-bearing moscovite-granite has the following composition :

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.
72·56	14·81	0·84	1·19	0·20	4·94	5·30	0·70	100·54

L. J. S.

**Beryl from Bosnia.** By FERDINAND KOCH (*Wiss. Mitth. aus Bosnien u. d. Hercegovina*, 1902, 8, 427—436).—A detailed description is given of crystals of beryl which occur in pegmatite in the Motajica planina mountains. The crystals exhibit optical anomalies. Analyses gave I for bluish-green and II for colourless crystals :

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	BeO.	Fe <sub>2</sub> O <sub>3</sub> (FeO).	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Loss on ignition.	Total
I.	65·73	14·58	11·48	2·84	0·32	0·45	0·39	0·77	0·19	2·53	99·28
II.	65·68	14·69	11·55	2·68	0·31	0·43	0·32	0·68	0·18	2·36	99·88

L. J. S.

**Analyses of Italian Bauxite.** By CARLO FORMENTI (*Gazzetta*, 1902, 32, i, 453—461).—The author states that samples of genuine bauxite have now been found in the province of Aquila in Southern Italy. The results of the physical and chemical examinations are given. The percentage of alumina present in the specimens varies from 51·13 to 57·52.

T. H. P.

[**Natron-phlogopite.**] By ERNST WEINSCHENK (*Zeit. Kryst. Min.*, 1902, 36, 317; from *Abhandl. Akad. Wiss. München.*, 1900, 21, 272).—In an account of the graphite deposits of Styria, the following analysis (by L. Wunder) is given of a colourless mica from crystalline limestone. The mineral has, besides a perfect basal cleavage, also a prismatic cleavage, as in the “brittle micas”; the optic axial angle is small. Sp. gr. 2·84:

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MgO.	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
	44·74	30·63	2·59	5·92	1·58	2·32	6·09	5·85	99·72

L. J. S.

**Action of Copper Sulphate on Iron Meteorites.** By OLIVER C. FARRINGTON (*Amer. J. Sci.*, 1902, [iv], 14, 38—42).—Wöhler, in 1852, observed that certain meteoric irons are not capable of reducing copper sulphate; the same observation has been made by other authors, and the distinctions “active” and “passive” have thus come to be applied. The present author, however, finds that copper is deposited on freshly cleaned surfaces of many of the irons which have been described as passive. The time (1 to 4 minutes at 18°) which elapses before copper is deposited varies with the amount of nickel present in the iron and with the temperature, but is independent of the concentration of the solution.

L. J. S.

**Meteorite from Admire, Kansas.** By GEORGE P. MERRILL (*Proc. U.S. National Museum*, 1902, 24, 907—913).—Several masses of this meteorite, weighing in the aggregate about 30 kilograms, have been ploughed up at Admire in Lyon Co. Sp. gr. 3·95—4·2. Angular fragments of olivine are set in a base, forming about one-third of the whole mass, of nickel-iron; schreibersite, troilite, chromite, and lawrencite are also present. Veins of the metallic minerals penetrate cracks in the olivine. The following analyses are given: I, nickel-iron; II, olivine; III, chromite.

	Fe.	Ni.	Co.	S.	P.	Cu.
I.	93	6	0·02	0·03	0·025	trace
	SiO <sub>2</sub> .	Cr <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	Total.	
II.	39·14	—	13·185	47·63	99·955	
III.	0·50	65·49	33·00	0·40	99·39	



The metallic constituents, which have clearly been introduced subsequent to the shattering of the olivine, have probably been derived from the lawrencite and troilite.

L. J. S.

**Meteoric Stone from Zavid, Bosnia.** By FRIEDRICH BERWERTH (*Wiss. Mitth. aus Bosnien u. d. Hercegovina*, 1902, 8, 409—426).—On August 1st, 1897, there was a fall of meteoric stones near Zavid in the Zvornik district; four stones were found, the largest of which weighed rather more than 60 kilograms. The stone is chondritic and consists largely of olivine and bronzite; it contains also a monoclinic pyroxene (?), plagioclase, glass, troilite, chromite and nickel-iron. A bulk analysis of the stone by C. Hödlmoser gave:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	S.	Fe.	H <sub>2</sub> O.	Total.
41.90	1.92	27.40	4.60	22.79	1.05	0.41	1.01	0.15	0.39	101.62

L. J. S.

**Alkaline Waters from the Lower Greensand.** By WALTER W. FISHER (*Analyst*, 1902, 27, 212—217).—Waters from the greensand, where the latter is exposed, are generally good and soft in character. The total solids, chlorine, and organic matter are sometimes quite small, whilst notable quantities of nitrates and iron are occasionally present. In the counties of Oxford and Buckingham, the greensand, and the Portland beds which underlie it, both gradually dip beneath the gault clay, and the water is here reached by deep borings. This water is materially different from that obtained from the uncovered beds. It contains considerable quantities of alkali chlorides, sulphates, and carbonates; the amount of nitrates is small, but the ammonia is large. The composition and quantity of the mineral constituents, however, was found to vary, even in wells a few miles apart. This is due to the fact that in places the water escapes by natural outlets, causing continual percolation through the beds and removal of soluble constituents.

W. P. S.

### Physiological Chemistry.

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The Effect of Decompression on the Respiratory Exchange of Man. By J. Tissor (*Compt. rend.*, 1902, 134, 1255—1258).—The respiratory exchanges were studied in the human subject, placed in a suitable chamber from which the air could be exhausted. It was found that decompression, until the pressure falls to 280 mm., does not alter the respiratory quotient during rest. The *apparent* respiratory debit (volume expired measured at the actual pressure and temperature) remains normal, but the *real* volume (measured at 0° and 760 mm.) diminishes with the pressure. The total quantity of carbon dioxide expired varies but little.

W. D. H.

**Disappearance of Ethers in the Blood in Vitro.** By MAURICE DOYON and ALBERT MOREL (*Compt. rend.*, 1902, 135, 54—56).—The ethereal extract of the serum does not, under aseptic conditions, decrease on keeping at 37°, but that of the whole blood does diminish; there is, however, no appearance of equivalent quantities of free fatty acids or of glycerol. The amount of free organic acid does increase slightly. The action is therefore not a lipolytic one. W. D. H.

**Does Lipase Exist in the Blood?** By MAURICE DOYON and ALBERT MOREL (*Compt. rend.*, 1902, 134, 1254—1255).—The non-existence of lipase in the blood is shown by experiments similar to those used in previous experiments with serum (this vol., ii, p. 464); that is to say, no diminution of alkalinity occurs when the blood (of dog) is mixed with oil and sodium carbonate. It is, however, necessary that such experiments should be conducted aseptically. W. D. H.

**Lipase in the Blood.** By MAURICE HANRIOT (*Compt. rend.*, 1902, 134, 1363—1365. Compare Abstr., 1901, ii, 562).—The correctness of statements of Doyon and Morel (see preceding abstract) is admitted, but the non-saponification of oil added to the blood is not regarded as proving the non-existence of lipase. W. D. H.

**Gastric Digestion in New-born Dogs.** By W. GMELIN (*Pflüger's Archiv*, 1902, 90, 591—616).—The stomach of new-born dogs contains neither pepsin nor rennin. These ferments appear together about the eighteenth day of life, and increase in amount and activity as the principal cells of the glands develop. The pancreatic juice also does not clot milk; this power appears at the same time as the gastric rennet. Trypsin, however, is present at birth, and is active; the size of the pancreas is relatively great in young animals.

In this early period, the acid in the gastric juice is lactic acid; this causes a flocculent precipitation of caseinogen. Hydrochloric acid appears later. When rennet first appears, it precipitates casein from dog's milk more readily than from cow's milk. Dog's caseinogen dissolves easily and completely in dilute lactic acid. W. D. H.

**Digestion in the Small Intestine. (II.)** By FRIEDRICH KUTSCHER and JOHN SEEMANN (*Zeit. physiol. Chem.*, 1902, 35, 432—458).—In the intestinal wall during absorption, it is possible to discover extractives which give no biuret reaction, and which on treatment with boiling acids yield leucine. The dead intestinal wall is capable of self-digestion; in this it resembles other organs rich in leucocytes. The intestine secretes an enzyme which acts feebly on fibrin, but more strongly in deutero-proteose. A direct measure of the intensity of deutero-proteose decomposition can be obtained by the use of the polarimeter. The importance of the proteolytic enzyme (O. Cohnheim's erepsin) in the normal digestion of proteid nutriment is considered to be small. W. D. H.

**The Presence of Erepsin in the Intestinal Juice of Dogs.** By SERGEI SALASKIN (*Zeit. physiol. Chem.*, 1902, 35, 419—425).—Cohn-

heim left the question open whether erespin acts intracellularly or is actually excreted in the succus entericus. The present research shows that it does occur in the juice in dogs. The idea, which originated with Cohnheim, and was confirmed by Kutscher and Seemann, that proteid is absorbed in the form of simple products is supported. The recent work of Glaessner, who supported Hofmeister's doctrine that 'regeneration of albumin' is the result of synthesis of proteoses and peptone, is criticised.

W. D. H.

**Proteid Digestion and Absorption in Octopods.** By OTTO COHNHEIM (*Zeit. physiol. Chem.*, 1902, 35, 396—415).—Proteid digestion in octopods yields the same products as in mammals. The blood, even during full digestion, does not contain these products; the only nitrogenous substance there is hæmocyanin. Proteid is absorbed wholly as simple products of its decomposition (leucine, tyrosine, lysine, arginine, ammonia). It is probable that the same is true for vertebrate animals also.

W. D. H.

**Mechanism of Intestinal Absorption in Octopods.** By OTTO COHNHEIM (*Zeit. physiol. Chem.*, 1902, 35, 416—418).—The study of absorption, especially of sodium iodide in octopods, lends support to the doctrine of cellular activity as opposed to mere physical diffusion. The process occurs through the intestinal wall. The liver of these animals does not participate in the process of absorption.

W. D. H.

**Formation of Sugar in the Liver during Perfusion of Blood through it.** By FRIEDRICH KRAUS, jun. (*Pflüger's Archiv*, 1902, 90, 630—634).—Increase of sugar occurs in the blood perfused through a dog's liver, especially if the liver contains much glycogen. It does not matter whether a solution of Witte's peptone is mixed with the blood or not. No change is noticeable in the proteoses or peptone if this mixture is used.

W. D. H.

**Human Bile.** By J. BRAND (*Pflüger's Archiv*, 1902, 90, 491—522).—Analyses are given of human fistula bile from nine cases of operation. The results are compared in tabular form with those previously recorded. The daily quantity varies from 500 to 1100 c.c., but the flow varies also from hour to hour; it falls in the night, reaches a minimum in the early morning, then rises and reaches a maximum soon after midday; sometimes a second maximum occurs in the evening. If the fistula is incomplete, the bile contains more solid material; this is explained by absorption of the bile salts in the duodenum, and re-secretion by the liver. The bile is also thickened by secretions of the bile-passages. The percentage of solids varies from 1 to 4 for fistula bile to 20 for bladder bile. The amount of organic constituents varies with the total metabolism. It is suggested that normal liver bile might be obtained by administering as much bile salts into the intestine daily as is lost by the fistula. The colouring matters of human bile are bilirubin, urobilinogen, and hæmatoporphyrin (in some cases). The reaction is neutral or alkaline; this

depends on, but is not quite parallel to, the mucous secretion. Sulphur in the form of ethylsulphuric acid is present to the extent of 6·4, and in the form of taurocholate to the extent of 11·7 per cent. of the solids (0·00077 and 0·0015 per cent. respectively of the fluid bile). Once taurocholic acid was absent; in the other cases, the relation of sodium taurocholate to glycocholate varied from 1 to 4·5—5·4. The molecular concentration of both fistula and bladder bile is about equal to that of the blood; the more concentrated bile contains larger molecules of specific bile constituents and less inorganic salts. In the gall-bladder and bile ducts, a saline solution isotonic with blood is absorbed, and mucin molecules were exchanged for salt molecules. A high percentage of mucin is usually associated with a high percentage of salts; the reason of this is not clear. Bile conducts electricity better than the blood on account of its higher percentage of salts (including organic salts).  
W. D. H.

**The Bile of the Isabella Bear.** By LEO VON ZUMBUSCH (*Zeit. physiol. Chem.*, 1902, 35, 426—431).—Some details of the character of this animal are given in order to compare them with the results obtained by Hammarsten on the bile of the polar bear. The presence of most of the usual constituents of bile is affirmed. The bile acid, however, comes nearest in its composition to the choleic acid of Lassar-Cohn.  
W. D. H.

**The Circulation of the Bile Acids.** By ALFRED C. CROFTAN (*Pflüger's Archiv*, 1902, 90, 635—639).—The bile acids which circulate in the blood are not discoverable in either the red corpuscles or the serum. It is believed that they are combined with the leucocytes; this is supported by the ease with which they can be detected in the leucocyte-rich fluid of the thoracic duct. Small quantities of bile acids in the blood act cytolytically, influence coagulation-time, and are cholagogues and vaso-dilatators. Whether they act under physiological conditions in any or all of these ways is uncertain.  
W. D. H.

**Is Alcohol a Food or a Poison?** By KASSOWITZ (*Pflüger's Archiv*, 1902, 90, 421—460).—The paper contains a good deal of controversial matter, and an account of experiments of a metabolic kind. The practical conclusion drawn is that alcohol is a poison, not a food, and should never be employed either in health or sickness.  
W. D. H.

**A New Proteid from the Brain.** By C. ULPANI and G. LELLI (*Gazzetta*, 1902, 32, i, 466—473).—The authors have separated from horse's brain a substance which they find to be a compound of protagon and paranuclein. Until broken up by alcohol, the compound does not yield protagon when treated with chloroform, which readily dissolves it in the free state.  
T. H. P.

**Auto-regulation of "Energetic" Functions by Carbon Dioxide.** By RAPHAEL DUBOIS (*Compt. rend.*, 1902, 135, 58—60).—Carbon dioxide is not to be regarded as a mere excretion, but as an antidote to oxygen, restraining various 'energetic' functions.  
W. D. H.

**Formation of Glycogen.** By OSCAR SIMON (*Zeit. physiol. Chem.*, 1902, 35, 315—323).—Those proteids which contain a carbohydrate radicle are capable of acting as parent substances of glycogen. The opinion, however, has been expressed that possibly other parts of the proteid complex might be converted into carbohydrate, and some rather contradictory experiments with leucine suggest that it may play this rôle. To test this question, the present experiments on rabbits were undertaken; the animals were rendered glycogen-free by means of strychnine, but subsequent administration of leucine never led either directly or indirectly to the formation of glycogen in either the liver or the muscles.

W. D. H.

**The Synthesis of Hippuric Acid in the Animal Organism.** By E. BASHFORD and W. CRAMER (*Zeit. physiol. Chem.*, 1902, 35, 324—326).—Bunge and Schmiedeberg were the first to show that the synthesis of hippuric acid from glycine and benzoic acid was accomplished by the kidney cells. The present experiments show that in the presence of oxygen at high pressure the same synthesis is accomplished by the thoroughly disintegrated and crushed kidney. The action is therefore not dependent on the life of the kidney cells, but is of a chemical nature. Whether it is the expressed juice that has this action, or whether the presence of red corpuscles as oxygen carriers is essential, are points not yet settled.

W. D. H.

**Human Semen.** By B. SLOWTZOFF (*Zeit. physiol. Chem.*, 1902, 35, 358—363).—The ash and dry residue in human semen are fairly constant; the amount of proteid averages 2.26 per cent. The proteids present are nucleo-proteid, mucin, albumin, and a substance with the characters of a primary proteose. The high percentage of calcium and phosphoric acid explains the frequent occurrence of calculi of calcium phosphate in the prostate.

W. D. H.

**Composition of Sheep's Milk.** By AUGUSTE TRILLAT and FORESTIER (*Compt. rend.*, 1902, 134, 1517—1519).—The milk of the sheep is richer in caseinogen, fat, and ash than that of the cow. The following table gives in percentages the mean of the analyses; the character of the soil is also given:

	Granitic.	Schistose.	Clay and chalk.	Chalk.
Butter.....	7.40	7.42	6.98	7.18
Lactose .....	5.37	5.35	5.53	5.26
Caseinogen .....	6.18	5.87	5.54	5.12
Ash.....	1.02	0.93	0.96	1.02
Lime .....	0.25	0.26	0.25	0.24
Acidity .....	3.70	3.00	2.66	2.8

W. D. H.

**Influence of Choline on Secretions.** By ALEXANDRE DESGREZ (*Compt. rend.*, 1902, 135, 52—54).—Choline is not a mere excretion. In addition to its favourable action on metabolism, it, like pilocarpine, provokes an increase in the secretion of saliva, pancreatic juice, bile, and urine. This is attributed to its trimethylamine group.

W. D. H.

**Oxalic Acid in Urine.** By WILHELM AUTENRIETH and HANS BARTH (*Zeit. physiol. Chem.*, 1902, 35, 327—342).—The best method for estimating oxalic acid in urine, faeces, or organs is a combination of precipitation and extraction processes, which is described in full. Oxalic acid is a normal and probably constant constituent of human urine; the opposite statement is due to the use of imperfect methods. The greater part of the acid is formed in the organism. Among pathological conditions, tubercle of the lungs and peritoneum and pernicious anæmia are those in which the formation of oxalic acid was found to be specially increased. In the rabbit, if oxalic acid is given, it is completely, or almost completely, burnt in the body.

W. D. H.

**Suprarenal Diabetes.** By FRITZ BLUM (*Pflüger's Archiv*, 1902, 90, 617—629).—The suprarenal bodies contain a substance injection of which into the blood-stream leads to glycosuria. The substance which produces this effect is believed to be identical with the reducing substance which raises blood-pressure. Von Fürth's suprarenin and Parke-Davis' adrenalin produce the effect. The character of the glycosuria resembles that produced by medullary puncture, so that the suprarenal substance possibly acts through the liver. The relationship of this condition to human diabetes is discussed; so also is the question whether the suprarenal forms an internal secretion or removes toxic material from the body; the author inclines to the latter view.

W. D. H.

**Physiological Action of Extracts of Kidney.** By ERNEST GÉRARD (*Compt. rend.*, 1902, 134, 1248—1250).—Aqueous extracts of kidney have been shown by Gonnermann to be capable of hydrolysing certain amides and anilides. In the present research, the kidney was first freed from blood, and therefore it is shown that the hydrolysing agents come, not from the blood, but from the renal tissue. The hydrolytic action was shown to take place with glycogen, guaiacol, oxaluric acid, and lactose, but not with starch and inulin. The action is destroyed by boiling the extract; the precipitate produced by alcohol has the same action as the original extract.

W. D. H.

**Action of Lecithin on the Animal Organism.** By ALEXANDRE DESGREZ and ALY ZAKY (*Compt. rend.*, 1902, 134, 1522—1523. Compare *Abstr.*, 1901, ii, 518).—It is the base choline to which lecithin owes its property of retarding the elimination of phosphoric acid. Betaine also possesses, although to a less degree, the power of favourably influencing the elaboration of nitrogenous matters and the weight of the organism.

W. D. H.

**Properties and Nature of Mixtures of Toxins with their Antitoxins.** By T. DANYSZ (*Ann. Inst. Pasteur*, 1902, 16, 331—345).—Experiments with solutions of ricine and an antiricine serum obtained from the goat show that mixtures of minimum activity are not completely indifferent, but possess slight antitoxic or toxic properties, and sometimes are at the same time both toxic and anti-

toxic. The composition of the mixture of minimum activity differs for different animals. A mixture of minimum activity does not spontaneously become active, but may be rendered active by an agent which will destroy one constituent but not the other. Ricine is much less acted on than antiricine by both gastric and pancreatic juice, and hence mixtures of minimum activity are rendered active by digestion. It seems probable that the toxin and antitoxin do not form a single compound, but unite in different proportions to form a series of compounds. Neither of the constituents is destroyed in the process of combination. A. H.

**Venom of the Common Toad.** By C. PHISALIX and GABRIEL BERTRAND [*Compt. rend.*, 1902, 135, 46—48. By G. BERTRAND (*ibid.*, 49—51)].—The venom is best obtained by squeezing it out from the glands. If an alcoholic extract of the whole skin is made, all the poisonous substances pass into solution, but these are mixed with other materials. The toxic action is due to two principal substances; one, named *bufotalin*, is of resinoid nature; it is soluble in alcohol, and slightly so in water; it arrests the frog's heart in systole. The other, termed *bufotenin*, is very soluble in both water and alcohol; it has a paralysing influence. The substance *bufonin*, described by Faust, is extracted from the skin; it is merely cholesterol mixed with a little bufotalin. W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Variations in the Products formed by Pathogenic Bacteria.** By ALBERT CHARRIN and A. GUILLEMONAT (*Compt. rend.*, 1902, 134, 1240—1243).—The soluble products of certain bacteria (*B. pyocyaneus*), when injected intravascularly, cause immediate death, whilst those of other microbic agents (for instance, *B. tetanus*, *B. diphtheria*) do not. The extreme toxicity is due, not to the pigments produced (these are not markedly poisonous), but to certain volatile compounds which are accessory to the true toxins. These volatile substances no doubt lower the resistance of the organism, so that it is more readily influenced by the toxins. The hæmolytic substances produced by one variety of bacillus are multiple; and, further, the numerous products are to some extent antagonistic towards each other. W. D. H.

**Nitrification in Different Soils.** By W. A. WITHERS and GEORGE S. FRAPS (*J. Amer. Chem. Soc.*, 1902, 24, 528—534. Compare Abstr., 1901, ii, 523).—The extent of nitrification of ammonium sulphate and cotton-seed meal in various soils, without and with addition of calcium carbonate, was determined. The conditions of moisture and temperature were known and the time was about three weeks.

As lending support to the view that ammonium sulphate hinders nitrification, it is mentioned that nitrification became more rapid when the amount of ammonium sulphate was reduced. The presence of calcium

carbonate was always beneficial, especially with ammonium sulphate. In some cases it was found that ammonium sulphate and in others that cotton-seed meal was the more rapidly nitrified. This is attributed to differences in the nitrifying microbes in the various soils. This view, although opposed to the prevailing opinion (Omeliansky, Abstr., 1900, ii, 97) that organic nitrogen has to be converted into ammonia before being nitrified, is in accordance with the results showing that the nitrous organism nitrifies organic nitrogen.

Continued application to limed soils of ammonium sulphate increases its power of nitrifying ammonium sulphate. N. H. J. M.

**Aërobic Fermentation of Farmyard Manure.** By C. DUPONT (*Ann. Agron.*, 1902, 28, 289—317).—*Bacillus mesentericus ruber* and *B. thermophilus Grignoni* are both oxidising bacteria which effect the combination of nitrogenous substances and carbohydrates; they produce carbon dioxide in large quantities and traces of volatile acids. The former is very active above 55° and can be cultivated in all media, even in absence of nitrogen; it attacks sugar and starch, and acts violently on proteids, with production of ammonia and liberation of some free nitrogen.

*B. thermophilus Grignoni* can exist at relatively very high temperatures. Its oxidising action resembles that of *B. mesentericus ruber*, except that it rarely produces ammonia from proteids.

Farmyard manure is very favourable to the growth of *B. mesentericus ruber*, which soon becomes the predominating microbe. As, however, the temperature rises its activity diminishes and it gives place to *B. thermophilus*, which will live at 70°. N. H. J. M.

**Production of Hydrogen Sulphide in Alcoholic Fermentation.** By M. EMM. Pozzi-Escot (*Bull. Soc. Chim.*, 1902, [iii], 27, 692—693).—From experiments on the production of hydrogen sulphide during fermentation in the presence of sulphur, the author finds that the reducing diastases are not set free until after the fermenting power has attained its maximum and the yeast ceases to grow freely.

A. F.

**Influence of Thiocyanic Acid on the Growth of *Aspergillus Niger*.** By AUGUSTE FERNBACH (*Compt. rend.*, 1902, 135, 51—52).—The addition of ammonium thiocyanate to Raulin's solution (0.1 to 0.5 gram per litre) does not prevent the growth of *Aspergillus niger*, but retards fructification, which does not take place until all the thiocyanate has been decomposed. C. H. B.

**Mode of Utilisation of Ternary Nourishment by Plants and Micro-organisms.** By PIERRE MAZÉ (*Ann. Inst. Pasteur*, 1902, 16, 195—232).—From a number of experiments on the germination of seeds, the conclusion is drawn that the carbohydrate reserve is first fermented to alcohol and carbon dioxide, and that the alcohol is then utilised for the production of tissue and the life of the seedling.

Thus when peas are exposed under water, in the absence of free oxygen, alcohol and carbon dioxide are produced, but no fresh living substance is produced; in the presence of oxygen, however, the alcohol is utilised for the production of ternary tissue. The fats of the seeds

are probably first converted into carbohydrates by absorption of oxygen, and these carbohydrates are then fermented in the same manner as those which occur in the seeds. A. H.

**Mode of Utilisation of Tertiary Carbon by Plants and Micro-organisms.** By PIERRE MAZÉ (*Ann. Inst. Pasteur*, 1902, 16, 346—378. Compare preceding abstract).—One of the ascomycetes, *Eurotysopsis Gayoni*, ferments sugars quite as readily as yeast and at the same time grows in a medium containing only mineral substances (including ammonium salts) and alcohol. A comparison of the modes of growth in solutions of dextrose and of alcohol shows that these are identical in principle and that in both cases it is the alcohol which is the primary compound assimilated. It seems probable, however, that it is not assimilated in this form, but is first oxidised with formation of aldehyde, which is then directly taken up by the protoplasm of the cells. A. H.

**Chlorophyll Assimilation.** By R. O. HERZOG (*Zeit. physiol. Chem.*, 1902, 35, 459—464).—Extracts crushed from green leaves in the same way as Buchner employed in making his extracts of yeast have no power to absorb carbon dioxide and give out oxygen. This confirms Engelmann's statement that this power of green plants depends on the chlorophyll granules being intact. W. D. H.

**Cyanogenesis in Plants. Part II. The Great Millet, *Sorghum vulgare*.** By WYNDHAM R. DUNSTAN and THOMAS A. HENRY (*Proc. Roy. Soc.*, 1902, 70, 153—154).—When young plants of *Sorghum vulgare* are crushed with water, hydrogen cyanide is produced (about 0.2 per cent. of the dried plant), owing to the action of a hydrolytic enzyme, apparently identical with emulsin, on a glucoside.

This glucoside, *dhuririn*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{CN})\cdot\text{O}\cdot\text{C}_6\text{H}_{11}\text{O}_6$ , crystallises readily and is soluble in alcohol or water. When hydrolysed by emulsin or dilute acids, it yields *p*-hydroxybenzaldehyde, dextrose, and hydrogen cyanide. If the glucoside is warmed with alkali hydroxide, it is converted into ammonia and *dhurric acid*; the acid, when heated with dilute hydrochloric acid, undergoes hydrolysis with formation of *p*-hydroxymandelic acid and dextrose. E. G.

**Analysis of Piper Famechoni or Kissi Powder.** By A. BARILLÉ (*Compt. rend.*, 1902, 134, 1512—1514).—The analysis of Kissi powder from Haute-Guinée (Africa) gave the following percentages :

Water.....	14.604	Proteids.....	10.253
Ash { soluble (3.61) }	4.550	Alcoholic extract .....	19.250
{ insol. (0.94) }		Aqueous extract .....	16.076
Volatile oil.....	4.470	Tannin .....	0.260
Piperine .....	3.654	Gummy, pectic, colour- ing, and nitrogenous matters .....	5.275
Starch.....	38.004	Resin, fixed oil .....	3.995
Cellulose.....	10.009	Total nitrogen .....	1.820
Dextrose .....	5.208		
Sucrose .....	1.663		

The powder is useful as a spice and condiment.

J. McC.

**Studies on the Feeding of Milch Cows and on the Relations of Milk Fat to Food.** By WHITMAN H. JORDAN, C. G. JENTER, and F. D. FULLER (*Bied. Centr.*, 1902, 31, 465—475; from *New York Agric. Exper. Stat. Bull.*, No. 197, 1901).—As regards the origin of milk fat, the conclusion is drawn that it is produced, at least in part, from carbohydrates. Increased, or, within certain limits, decreased amounts of proteids in the foods have no direct effect on milk production, but only result more or less in the decomposition of the digestible protein.

The heat value of urine is shown to have no relation to the amount of nitrogen. The value cannot be estimated, but should be determined in each case.

The distribution and utilisation of the heat value of food in milk production is as follows:—More than 40 per cent. of the available heat value is used for maintenance, whilst more than 30 per cent. goes to the solid constituents of the milk. The remaining quarter or fifth of the heat value is available for promoting the milk secretion.

N. H. J. M.

**Study of Rations Fed to Milch Cows in Connecticut.** By C. S. PHELPS (*Storr's Agric. Exper. Stat. 13th Ann. Rep.*, 1901, 130—157).—The experiments were made with four herds (two series each), and covered periods of 11—12 days. In the first series, the food was essentially the same for each cow, whilst in the second series the food was varied according to the yields of butter fat. Cows which yielded in the first series 50—65 lb. of butter fat received in the second series the basal ration only; whilst cows which had yielded 66—80 lb., 81—95 lb., and 95—100 lb. of fat in the first series received in addition to the basal ration respectively 1, 2, and 3 lb. of protein mixture, containing about 30 per cent. digestible protein.

The results illustrate the economy of feeding a larger proportion of protein than is usual. Rations supplying 1·80 to 2·60 lb. of digestible protein per day were generally more remunerative than those containing less protein.

N. H. J. M.

**Experiments on Feeding Pigs with Sugar, Rye Bran, and Meat Meal.** By J. KLEIN (*Bied. Centr.*, 1902, 31, 534—539; from *Milchzeit.*, 1901, *Heft* 6, 7, and 8).—Whilst sugar, rye bran, and meat meal were without injurious effect on the fat of pigs, meat meal had a marked effect on the flesh; the effect was, however, less than is sometimes stated.

N. H. J. M.

**Keeping Properties and Storage of Molasses Foods.** By BERNHARD SCHULZE (*Bied. Centr.*, 1902, 31, 539—546; from *Arb. deut. landw. Ges.*, 1901, *Heft* 59).—The liability of molasses foods to decompose increases with the amount of water. There may be a very serious loss of sugar and the cane sugar becomes inverted. Peat molasses undergoes no essential change unless the percentage of water is high; the amount of water should not exceed 30 per cent.

In preparing the foods, the molasses should be concentrated as much as possible, and addition of water is to be avoided.

N. H. J. M.

**Effect of Calcium Carbonate in the Soil on the Development of Leguminous Plants in Pots.** By BERNHARD SCHULZE (*Bied. Centr.*, 1902, 31, 455; from *Jahresber. agrik.-chem. Versuchs-Stat. Breslau*, 1900).—The soil was fully manured and received, in addition, 0.1–5.0 per cent. of pure calcium carbonate. The plants grown were peas, beans, vetches, and red clover.

On the whole, 1 per cent. of carbonate gave the best results, but the yields in the pots which had 5 per cent. were almost as good.

N. H. J. M.

**Pot Experiments on the Manurial Requirements of Silesian Soils.** By BERNHARD SCHULZE (*Bied. Centr.*, 1902, 31, 436–437; from *Jahresber. agrik.-chem. Versuchs-Stat. Breslau*, 1900).—The results of pot experiments showed in every case a very marked deficiency of phosphoric acid in the soils.

N. H. J. M.

**After Effect of Ammonium Sulphate.** By E. KLOEPFER (*Bied. Centr.*, 1902, 31, 438–440; from *Fühling's landw. Zeit.*, 1901, 154).—Oats were grown in 1900 on the experimental plots which had grown roots and potatoes (without and with ammonium sulphate) in 1899. In every case, the yield of oats was greater on the plots which received nitrogen in 1899 than on the others.

N. H. J. M.

**Effect of Straw, Peat, and Cow Dung, &c., on the Action of Nitrogen as Nitrates.** Alinit. By MAX GEBLACH (*Bied. Centr.*, 1902, 31, 435–436; from *Jahresber. Landw. Versuchs-Stat. Posen*, 1900–1901).—Addition of straw considerably reduced the effect of nitrates. Peat, when applied with nitrates, reduced grain production and increased straw production. Cow dung, with straw and nitrates, had almost no effect.

The application of carbon disulphide, in addition to straw and cow dung, resulted in a considerably increased growth.

Negative results were obtained with alinit.

N. H. J. M.

**Effect of Soil Moisture on the Action of Bone-meal as compared with Basic Slag and Superphosphate.** By CONRAD VON SEELHORST (*J. Landw.*, 1902, 50, 167–174).—The results of pot experiments on oats and clover showed that whilst the amount of water in the soil was without effect in the case of bone meal, an increased amount of water in the soil increased the activity of basic slag and superphosphate.

N. H. J. M.

**The Time for Manuring Peaty Meadows, especially with Potassium Salts.** By BRUNO TACKE (*Bied. Centr.*, 1902, 31, 507–509; from *Mitt. Ver. Förd. Moorkultur. Deut. Reiche*, 1902, 1).—Potassium salts should be applied when vegetation is dormant, rather than soon after the commencement of new growth, unless serious loss of potassium is to be feared, as when the meadows are flooded.

Forty per cent. potassium salts gave better results than kainite when applied in the spring, owing to the solution being less concentrated.

N. H. J. M.

**Value of Forty per cent. Potassium Salts as compared with Kainite.** By MAX MAERCKER and W. SCHNEIDEWIND (*Bied. Centr.*, 1902, 31, 505—507; from *Arb. deut. landw. Ges.*, 1902, Heft 67).—The results of field experiments on cereals, grown in both heavy and light soils, showed that kainite gave more satisfactory results than 40 per cent. potassium salts. In the case of potatoes, potassium salts gave the better results, both as regards the yield of tubers and starch production. The percentage amount of starch was lowered by potassium salts, but less than by kainite. Potassium sulphate gave very good results with potatoes.

In the case of high per cent. sugar beet, potassium salts are preferable to kainite, in the case of good soils, as larger amounts of potassium can be applied without injuring the mechanical properties of the soil.

N. H. J. M.

**Plot and Pot Experiments on the Value of Different Potassium Manures.** By BERNHARD SCHULZE (*Bied. Centr.*, 1902, 31, 449—453; from *Jahresber. agrik.-chem. Versuchs-Stat. Breslau*, 1900).—Potassium chloride considerably increased the yield of clover, whilst the yields with kainite and potassium sulphate were rather less than without manure. The crop contains, however, in each instance more potassium than when no manure was applied, especially in the case of potassium chloride. Potassium sulphate gave the least satisfactory results.

Pot experiments are described in which white mustard, oats, peas, and sugar beet were manured with the same amounts of potassium in different forms. The following percentage amounts of potash were utilised by the plants:

	Beet.	White Mustard.	Oats.	Peas.	Mean.
Kainite .....	22.1	20.0	11.0	20.0	18.0
Potassium sulphate...	43.9	60.0	29.0	60.0	48.0
„ chloride...	48.0	54.0	33.0	69.0	51.0

N. H. J. M.

**Manurial Experiments with Potassium on Sugar Beet in 1900.** By AUMANN (*Bied. Centr.*, 1901, 31, 447—449).—The results of experiments made near Hildesheim showed that about half the land required potash. Kainite gave better results when applied three times than when the whole was applied at the same time. The highest yield of sugar was obtained after manuring with 40 per cent. potassium salts.

N. H. J. M.

**Pot Experiments on the Action of Lime and Magnesia in Burnt Lime and Marls.** By RICHARD ULBRICHT (*Landw. Versuchs-Stat.*, 1902, 57, 103—166. Compare Abstr., 1900, ii, 240).—The experiments now described were made with barley. Whilst application of lime increased the yield, the weight of the grain was diminished by lime and marl (applied in February); the number of ears was increased.

Large amounts of magnesia lower the yield of grain, and still larger amounts the yield of straw as well. N. H. J. M.

Utilisation of Calcium Carbide Residues in Agriculture. By MAX GERLACH (*Bied. Centr.*, 1902, 31, 511—514; from *Fühling's Landw. Zeit.*, 1902, 81).—The material employed contained: water, 49.52; calcium hydroxide, 40.69; calcium carbonate, 7.33; insoluble in hydrogen chloride, 0.43 per cent. Traces of potassium and nitrogen were found, but no phosphoric acid. As a manure, its action resembles that of lime. N. H. J. M.

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### Analytical Chemistry.

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**New Reagent for the Detection of Ozone.** By GRIGORI V. CHLOPIN (*Zeit. Nahr.-Genussm.*, 1902, 5, 504—505).—Strips of ordinary filter-paper are dipped in a moderately concentrated alcoholic solution of a dye, sold under the name of "Ursol D," and dried. When moistened with water and exposed to the action of ozone, the strips are coloured blue. Hydrogen peroxide has no action on the test-papers, whilst nitrous fumes, chlorine, and bromine give a bluish-green coloration, soon changing to yellow. Carbon dioxide also has no action on the papers. The test-papers should be freshly prepared for use. W. P. S.

**Detection and Estimation of Minute Quantities of Hydrogen Sulphide in Coal-gas.** By WILLIAM J. DIBDIN and ROBERT GEORGE GRIMWOOD (*Analyst*, 1902, 27, 219—223).—Of all the reagents employed, dry lead acetate papers were found to afford the most sensitive means for detecting almost infinitesimal traces of hydrogen sulphide in coal-gas. To ascertain the smallest amount which could be detected, a known volume of hydrogen sulphide was introduced by means of a capillary tube into a large glass reservoir holding 15,500 c.c. of coal-gas. When diffusion had taken place, a toy balloon in the reservoir was partially inflated, causing some of the contaminated gas to pass into a bell-jar containing the strip of lead paper. The rate of flow of the gas was half a foot per hour, and, by diluting down the contents of the reservoir with fresh coal-gas, it was found that, within a reasonable time, 1 volume of hydrogen sulphide could be detected in 1,000,000,000 of coal-gas, or 1 grain in 600,000 cubic feet of gas. By regulating the distance of the lead paper from the nozzle and passing the gas at the rate of half a foot per hour, it was found that the time required for the production of a colour was constant for that proportion at that distance. Comparison of the colorations produced was not possible owing to the evanescent nature of the colour spot. W. P. S.

**Estimation of Uncombined Sulphur Dioxide in Fermented Beverages.** By MATHIEU and BILLON (*Ann. Chim. anal.*, 1902, 7, 252—256).—The total sulphur dioxide is estimated by de Haas'



distillation method. The combined sulphur dioxide (that in combination with aldehydes) is then estimated, the difference representing the free sulphur dioxide.

The combined acid is estimated as follows: 100 c.c. of the sample (wine, beer, cider, &c.) are introduced into de Haas' apparatus, previously filled with carbon dioxide: 2 c.c. of hydrochloric acid are added, and then a sufficiency of *N*/50 iodine; the exact amount necessary has been previously determined by adding the solution to 10 c.c. of the sample until a drop gives a decided reaction with starch. The iodine at once oxidises the free sulphur dioxide, but does not act on the combined acid in the cold; further action, however, is prevented by adding a corresponding amount of sodium arsenite. The liquid is now submitted to distillation, the distillate being received into an excess of iodine solution, and the sulphuric acid thus formed is then estimated and calculated to sulphurous acid.

As a check, the sulphates in the residue of the distillation in de Haas' and the authors' methods may be estimated. The difference represents the free sulphurous acid. L. DE K.

**Detection of Nitrates in the Presence of Alkali Ferro- and Ferri-cyanides.** By AUGUSTE F. LEUBA (*Ann. Chim. anal.*, 1902, 7, 258).—The solution is freed from ferro- or ferri-cyanide compounds by precipitating with a solution of cadmium chloride. To the filtrate, the usual test for nitrates with ferrous sulphate and sulphuric acid is then applied; it may also be tested for nitrites. L. DE K.

**Apparatus for the Analysis of Calcium Carbide.** By CARLO FORMENTI (*Chem. Centr.*, 1902, i, 1341; from *Boll. Chim. Farm.*, 41, 209—302).—About 3—5 grams of the calcium carbide are introduced into a weighed flask in which is placed a tube containing about 4 c.c. of brine; the flask is fitted with a calcium chloride tube and a bent tube reaching to the bottom. After weighing, the flask is slightly inclined so as to allow the brine to fall on to the carbide. When evolution of gas ceases, dry air is drawn through the apparatus, which is then reweighed; the loss represents acetylene. L. DE K.

**Simple Method for the Estimation of Iron in Metabolism Experiments.** By ALBERT NEUMANN (*Chem. Centr.*, 1902, i, 1422—1423; from *Arch. Anat. Phys.* [His-Engelmann] *Physiol. Abt.*, 1902, 362—365. Compare this vol., ii, 176).—The solution obtained as previously directed is mixed with 20 c.c. of a reagent prepared by precipitating a solution containing 25 grams of zinc sulphate with one containing 100 grams of disodium hydrogen phosphate, dissolving the precipitate by addition of dilute sulphuric acid, and diluting to 1 litre. Ammonia is now added until the precipitate has nearly all redissolved and the solution is then boiled; the crystalline zinc precipitate carries down every trace of iron. The precipitate is washed by decantation, dissolved in hydrochloric acid, and after neutralising the excess of acid with ammonia the iron is titrated as usual by means of potassium iodide and *N*/250 thiosulphate solution.

When dealing with liquids such as urine, it is now recommended to first add one-tenth volume of strong nitric acid and then gradually drop 100 c.c. of the mixture into 30 c.c. of boiling nitric acid; after evaporating to 50 c.c., the usual mixture of nitric and sulphuric acids is added and the operation conducted as before.

L. DE K.

**New Method for the Precipitation and Separation of Thorium Earths.** By A. KOLB (*J. pr. Chem.*, 1902, [ii], 66, 59—64).—Thorium is precipitated from a solution of its chloride or nitrate by water saturated with aniline, whilst the chlorides or nitrates of cerium, lanthanum, didymium, yttrium, and erbium are not precipitated. Any colouring matter (from the aniline) which the precipitate contains can be removed by ignition.

R. H. P.

**Estimation of Vanadium.** By H. CORMIMBŒUF (*Ann. Chim. anal.*, 1902, 7, 258—260).—A modification of Roscoe's method. The alkaline solution containing the vanadic acid is acidified with acetic acid and precipitated with lead acetate, and the precipitate is collected on a tared filter, washed with water containing a little acetic acid, dried at 100°, and weighed. As it contains a slightly variable amount of lead, it is removed from the filter, and after having been well mixed in a mortar, an aliquot part is dissolved in water containing a little nitric acid and the lead is precipitated by adding sulphuric acid. (In Roscoe's original process, the lead sulphate is weighed, calculated to lead oxide, and deducted from the lead vanadate, the difference being vanadic acid.) The filtrate is evaporated in a weighed porcelain dish, and the residue gradually heated to expel the sulphuric acid, and finally heated to redness; the vanadic acid is then obtained as a partially fused mass.

L. DE K.

**Estimation of Organic Nitrogen in Water.** By HENRI CAUSSE (*Compt. rend.*, 1902, 134, 1520—1522).—The method of estimating the nitrogen is as follows:—25 c.c. of a saturated solution of barium hydroxide containing 20 per cent. of barium chloride are added to a litre of water and the mixture is left for one day. The precipitate which forms is collected and washed, then mixed with twice its volume of a 10 per cent. solution of potassium carbonate, and heated on the water-bath for 20—25 minutes. The clear liquid is decanted through a filter, and the residue treated again in the same way with half the quantity of the potassium carbonate solution. The filtrates are united and made acid with sulphuric acid, then evaporated to dryness. The dry residue is heated with 5 c.c. of sulphuric acid and the organic matter destroyed in the usual way. One hundred c.c. of distilled water are added and the liquid heated to boiling to expel the sulphur dioxide. After cooling, potassium hydroxide is added in excess and 25 c.c. are distilled off. The mixture is allowed to cool and another 25 c.c. are distilled off; the two fractions are united, made up to 100 c.c., and the ammonia determined by the Nessler method.

The author gives some results of the determination with Rhone water at different periods, and discusses the question of organic nitrogen and potability.

J. McC.

**Influence of Potassium Ferrocyanide on the Precipitation of Phosphoric Acid by Molybdate Solution.** By AUGUSTE F. LEUBA (*Ann. Chim. anal.*, 1902, 7, 257).—In the presence of ferrocyanide, a dense, reddish-brown precipitate is formed, completely obscuring the yellow phosphomolybdate precipitate. It is, however, readily soluble in a solution of sodium carbonate, and on carefully neutralising this with nitric acid and gentle warming, the yellow precipitate will duly appear. L. DE K.

**Estimation of Glycerol.** By SIMON ZEISEL and R. FANTO (*Chem. Centr.*, 1902, i, 1424—1425; from *Zeit. landw. Versuchs-Wes. Oesterr.*, 5, 729—745. Compare this vol., ii, 111).—The substance is distilled in a special apparatus with hydriodic acid containing from 57 to 63 per cent. of hydrogen iodide in a current of carbon dioxide. The vapours, cooled to 60°, are passed through a small wash-bottle containing amorphous phosphorus suspended in water at 60° to free them from iodine or hydrogen iodide. The isopropyl iodide formed by the action of the hydriodic acid on the free or combined glycerol is finally passed through a 4 per cent. alcoholic solution of silver nitrate, and the silver iodide formed is collected and weighed. Its weight multiplied by 0.3922 gives the amount of glycerol. L. DE K.

**Delicate Reaction for Dextrose and other Aldehydes.** By EM. RIEGLER (*Ann. Sci. Univ. Jassy*, 1901, 1, 256—258).—A solution of dextrose, treated with small quantities of phenylhydrazine hydrochloride and sodium acetate, is heated to boiling and rendered alkaline with sodium hydroxide solution; the mixture is then shaken several times and allowed to remain until a reddish-violet coloration is developed. This change takes place immediately if the solution contains more than 5 per cent. of the sugar, but in any case the coloration appears within 15 minutes, the colour being distinct even in 0.003 per cent. solutions. A sample of urine containing a pathological amount of dextrose should give the coloration in one minute at the latest.

Formaldehyde or acetaldehyde may also be detected in a similar manner by adding their solutions to a mixture of phenylhydrazine hydrochloride suspended in aqueous sodium hydroxide solution. A reddish-violet coloration is developed either by boiling or by prolonged agitation. The presence of formaldehyde in milk may be ascertained by this process. G. T. M.

**The Osazone Test for the Detection of Sugar in Urine.** By FRIEDRICH ESCHBAUM (*Chem. Centr.*, 1902, i, 1253; from *Apoth. Zeit.*, 17, 280—282).—Five drops of phenylhydrazine, 20 drops of acetic acid, and 50 drops of the suspected urine are boiled in a test-tube for just one minute in a fume chamber. A quantity of aqueous sodium hydroxide slightly less than is wanted for complete neutralisation is added, the mixture is again heated to boiling, and then allowed to cool. After some time, the clear liquid is decanted and the deposit examined microscopically for phenylglucosazone. This forms tufts of yellow needles; other crystalline forms are not characteristic for sugar.

0.025 per cent., and, in the absence of much uric acid, even 0.01 per cent. of dextrose may thus be detected. L. DE K.

**Estimation of Glycogen.** By EDUARD PFLÜGER (*Pflüger's Archiv*, 1902, 90, 523—524).—Glycogen purified by the Brücke-Külz method is rapidly decomposed by warming with dilute alkali. If, however, the glycogen is obtained without the use of mineral acids or Brücke's reagent, it can be heated for many hours with strong alkali without undergoing any change. If flesh containing glycogen is boiled with 30 per cent. potassium hydroxide, the same yield is obtained whether the boiling be continued for 1 or 24 hours. The material which has hitherto been termed glycogen is only a decomposition product of true glycogen, and the name pseudo-glycogen is suggested for it. Glycogen is obtained from flesh by precipitating it with alcohol from an alkaline extract containing potassium iodide. It is then boiled and inverted and the final estimation made by Volhard's method. Further details are promised. W. D. H.

**Estimation of the Tartaric Acid in Wines.** By LOUIS MAGNIER DE LA SOURCE (*Ann. Chim. anal.*, 1902, 7, 246—249).—The conventional (French) method is to determine the amount of potassium hydrogen tartrate after adding a little potassium bromide to the sample. In another portion of the sample, the existing potassium hydrogen tartrate is estimated, and the difference between the two determinations  $\times 0.8$  gives the amount of the free tartaric acid. This determination is made by one of three methods; (a) by mixing the sample with alcohol and ether; (b) by adding alcohol, ether, and tartaric acid; (c) by evaporation, preferably in a vacuum.

The author states that method (a) is utterly untrustworthy and has caused great discrepancies in wine analyses; (b) and (c), however, give trustworthy and concordant results. L. DE K.

**The Determination of Iodine Absorption by Means of Iodine Monochloride.** By J. J. A. WIJS (*Zeit. Nahr.-Genussm.*, 1902, 5, 497—504).—The solution of iodine monochloride in glacial acetic acid keeps well, provided that the purest acetic acid is employed. The presence of iodine trichloride, water, or traces of alcohol causes the solution to diminish in strength from day to day. Carbon tetrachloride should be used in place of chloroform, as the latter frequently contains alcohol. Ordinary Hübl's solution is similarly affected by the presence of water and aldehydes in the alcohol used in its preparation. When a 70 per cent. excess of iodine is employed, the results obtained by the use of iodine monochloride agree closely with those required by theory, especially in the case of unsaturated fatty acids having one double-linking. W. P. S.

**Analysis of Butter.** By A. KICKTON (*Zeit. Nahr.-Genussm.*, 1902, 5, 458—459).—Attention is drawn to the advisability of applying the phytosterol acetate test to butters which give a low Reichert-Meissl number and yield negative results with the usual tests for cotton-seed and sesamé oils. W. P. S.

**Estimation of Lecithin in Milk.** By FRED. BORDAS and SIG. DE RACZKOWSKI (*Compt. rend.*, 1902, 134, 1592—1594).—Stoklasa's method (*Abstr.*, 1897, ii, 573) of estimating lecithin in milk, which consists in determining the phosphoric acid present in the alcohol-ether extract of the dry residue of a given quantity of milk, and then multiplying by a factor to obtain the amount of lecithin, is shown in the first place only to hold approximately if the latter is regarded as present in the form of lecithin oleo-margarate; and secondly, incineration of the alcohol-ether extract with potassium carbonate and nitrate does not effect the complete conversion of the phosphorus into phosphate. The authors recommend an estimation of the phosphate, and hence a determination of the phosphoglyceric acid. The method employed is as follows: 100 c.c. of milk are added to a mixture of 100 c.c. of alcohol and 100 c.c. of water and 10 drops of acetic acid; the coagulum is collected and washed three times with 50 c.c. of boiling alcohol; this extract is evaporated to dryness and the residue taken up in alcohol-ether and then hydrolysed with potassium or barium hydroxide; the soap is decomposed by nitric acid, the fatty acid filtered off, and the phosphoglyceric acid in the filtrate oxidised to phosphate by concentrated nitric acid and permanganate; the phosphate is finally weighed as magnesium pyrophosphate; when the quantity of the latter is multiplied by the factor 1.5495, the amount of phosphoglyceric acid in 100 c.c. of milk is obtained. K. J. P. O.

**Evaluation of Gelatin and Glues.** By ARTHUR MÜLLER (*Zeit. angew. Chem.*, 1902, 15, 482—487).—The process is briefly as follows:—Ten grams of the sample are soaked in water and finally dissolved by heating on the water-bath; after diluting to 500 c.c. with water at 30°, three separate portions of 10 c.c. are pipetted off, and to each are added 25 or 30 c.c. of tannin solution (3), and then, after vigorous stirring, 20 c.c. of alum solution (4). The precipitates are well washed with water at 30°. The three filtrates are then treated as follows: The first is mixed in a closed flask with 2 grams of hide powder and put away for 18 hours, when the liquid is passed through a filter and the hide powder well washed. The filtrate is then titrated by the method proposed by Gantter (*ibid.*, 1889, 517), as modified by Schroeder and Paessler (*Zeit. anal. Chem.*, 1890, 29, 698).

(This process differs from the ordinary permanganate process in so far that the permanganate solution (1) is allowed to act at boiling point; standard oxalic acid (2) is then added and the excess again titrated with permanganate.)

The second filtrate is mixed with 20 c.c. of dilute sulphuric acid (1:5) and titrated as described. The third portion is then titrated, 3 c.c. of acid being added for every 5 c.c. of permanganate consumed in the second titration. The difference between the result of the first and third titrations gives the amount of permanganate consumed by the excess of tannin only. The tannin solution (3) is also checked with permanganate; 5 c.c. of the solution and 12 c.c. of dilute sulphuric acid are titrated at boiling point with permanganate as described, and the operation is repeated with 5 c.c. previously treated with hide powder. By an easy calculation, it is found how much of the added

tannin has been precipitated by the gelatin. If the directions are scrupulously followed, 100 parts of pure tannin correspond with 139.1 parts of glutin. For isinglass, the figure lies between 144.6 and 145.

*Preparation of the Solutions.*—(1) 5.7469 grams of pure potassium permanganate are dissolved to 1 litre. (2) 11.4573 grams of chemically pure oxalic acid dissolved to 1 litre. (3) A solution made by dissolving 5 grams of pure tannin to 1 litre. (4) A 5 per cent. solution of pure potash-alum which should not consume any permanganate.  
L. DE K.

**Detection of Gelatin and Gelose in Jams.** By A. DES-  
MOULIÈRE (*Ann. Chim. anal.*, 1902, 7, 201—204).—Gelatin is sought for, as usual, by adding excess of alcohol and testing the precipitate with tannin, picric acid, and quick-lime (? soda-lime). Gelose is tested for as follows: 30 grams of the sample are heated with 10 c.c. of water and 150 c.c. of strong alcohol are added. After 12 hours, the liquid is decanted and the deposit is dissolved in 50 c.c. of water and boiled for a few minutes. Lime-water is added until the solution is strongly alkaline to litmus paper, the liquid is passed through a fine cloth which retains the calcium pectate, and the solution is now rendered nearly neutral by means of oxalic acid. After concentrating the liquid to 30 c.c., 2 c.c. of commercial formaldehyde are added and the whole is evaporated to dryness. The residue is then boiled with 50 c.c. of water and filtered through a hot-water funnel. (In the absence of gelatin, the addition of formaldehyde and subsequent evaporation may be dispensed with.) The filtrate is finally evaporated to about 7 c.c. and then allowed to cool. If gelose is present, the solution will be more or less gelatinised.  
L. DE K.

**Estimation of Diastases; Colorimetric Estimation of Oxydases.** By HENRI ALLIOT and M. EMM. POZZI-ESCOT (*Ann. Chim. anal.*, 1902, 7, 210—212).—The authors have found it impossible to estimate oxydases colorimetrically either by Laborde's guaiacol method, or Kastle and Schedd's phenolphthalein process (this vol., i, 514).  
L. DE K.

**Composition and Volumetric Estimation of Sodium Methylarsinate.** By ALPHONSE L. ADRIAN and J. AUGUSTE TRILLAT (*Compt. rend.*, 1902, 134, 1231—1232).—Sodium methylarsinate has the composition  $\text{Na}_2\text{MeAsO}_3 \cdot 6\text{H}_2\text{O}$ . In order to estimate this compound, it is precipitated with a slight excess of standard silver nitrate solution, filtered, and the excess of silver determined by means of standard thiocyanate solution. A correction must be made on account of the solubility of silver methylarsinate; 50 c.c. of the saturated solution consume 0.5 c.c. of decinormal thiocyanate solution.  
C. H. B.

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## General and Physical Chemistry.

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**Refractive Indices of Solutions in Carbon Disulphide.** By CARL FORCH (*Ann. Physik.*, 1902, [iv], 8, 675—685).—The refractive indices of solutions of various concentrations of sulphur, naphthalene, ether, chloroform, paraffin oil, and castor oil in carbon disulphide have been determined. The value of the refractive indices of the chloroform solutions changes almost exactly proportionally with the dilution. The addition of naphthalene scarcely changes the refractive index of carbon disulphide. The results are given in the form of curves.

J. McC.

**Spectra arising from the Dissociation of Water Vapour and the Presence of Dark Lines in Gaseous Spectra.** By JOHN TROWBRIDGE (*Phil. Mag.*, 1902, [vi], 4, 156—161).—When a tube containing hydrogen and a little air and water is subjected to a powerful discharge, a spectrum is obtained which shows, besides hydrogen, sodium (from the glass), dissociated water vapour, and argon.

The spectrum of a spark under water has been photographed and is continuous, and this is the dissociation spectrum of water under pressure. Plücker or Geissler tubes subjected to a powerful discharge give a faint continuous spectrum on which there are bright and dark lines in the photograph. The dark lines are not due to absorption by cooler layers of gas, but are attributed to the silver salt not being able to record an effect for this particular state of vibration, and this phenomenon increases in intensity with the temperature.

From the study of a photograph of the solar spectrum, the author concludes that oxygen is present in the atmosphere of the sun and that dissociation of water vapour takes place there.

J. McC.

**Rotation Dispersion of Spontaneously Active Substances.** By CHR. WINTHER (*Zeit. physikal. Chem.*, 1902, 41, 161—211).—The rotation of dimethyl, diethyl, and dipropyl tartrates in the pure state has been determined for red, yellow, green, light blue, and dark blue light, and at several temperatures. The rotation dispersion is anomalous in each case, but the dispersion curves of the three esters, that is, the curves showing the variation of the specific rotation with the wavelength of the light employed, form a continuous series; the form of the dispersion curve changes gradually either with rise of temperature or increase of molecular weight, the change being apparently the same in either case; thus the dispersion curve for diethyl tartrate at 70° is practically coincident with that for dipropyl tartrate at 20°. The variation of the specific rotation of the esters with temperature is in accordance with the equation  $[\alpha] = a - b(t - 149)^2$ ; 149° is the calculated temperature at which all the esters have the maximum value of rotation. The specific rotation, wave-length, and temperature are connected by the equation

$$[\alpha] = (c - d\lambda)/(\lambda - e) \cdot [(f\lambda - g)/(\lambda - h) - (t - 149)^2],$$

in which  $c$ ,  $d$ ,  $e$ ,  $f$ ,  $g$ , and  $h$  are constants: according to the author, this dispersion formula gives values more in accordance with experiment than the Cauchy-Boltzmann formula.

The rotation of solutions of tartaric and malic acids has been determined, and the specific rotations of the acids themselves obtained by extrapolation; in the pure state and at low temperatures, these substances exhibit normal dispersion, but with rise of temperature or dilution the dispersion becomes anomalous, finally becoming normal again. The rotation of alcoholic solutions of tartaric acid has also been studied. For the range of concentrations chosen, the rotation values are much smaller than those in aqueous solution; the maxima on the dispersion curves lie between light and dark blue for the aqueous solutions, but between red and yellow for the alcoholic solutions; the rotation of the aqueous solutions diminishes rapidly, that of the alcoholic solutions increases slightly, with rising concentration.

The three esters referred to above, with tartaric and malic acids, are classed together in a group, the characteristics of which are anomalous dispersion and exceptionally large variation in the dispersion with temperature, concentration, and solvent. Sodium potassium tartrate, the rotation and dispersion of which were also studied, is an example of another class characterised by normal dispersion and slight variation in the dispersion with temperature and concentration.

If, in the case of the three ethereal tartrates, the rotation is measured, not from zero, but from the maximum rotation value above referred to, there is obtained what the author calls the "rational" specific rotation  $[A]$ : it is defined by the equations  $[A] = \alpha - [\alpha] = b(t - 149)^2$ ; if the temperature as measured from the maximum point  $149^\circ$  be termed 'rational' temperature ( $T$ ), then obviously  $[A] = bT^2$ . From the 'rational' specific rotation, a 'rational' dispersion coefficient is deduced in the usual manner, and it is shown that for the three esters, tartaric and malic acids, this dispersion coefficient is independent of temperature. For the homologous esters, the 'rational' dispersion coefficient is apparently constant.

J. C. P.

**Comparison of the Radiations from Radioactive Substances.** By E. RUTHERFORD and Miss H. T. BROOKS (*Phil. Mag.*, 1902, [vi], 4, 1—23).—The more penetrating  $\beta$ -radiation from uranium is deflected by a magnet, the deflection being of about the same order as for radium rays. The  $\alpha$ -radiation is not affected by a magnetic field. The coefficient of absorption of  $\beta$ -rays by various metals has been determined, and it is found that the law of the absorption of cathode rays depending only on the density is not true for all substances. The most penetrating rays are the excited radiations due to thorium and radium, then follow in order the rays from thorium, radium, polonium, and uranium. In seeking for a connection between absorption and density, it has been found that when aluminium and air are compared, the absorption is proportional to the density. The result for the non-deviable rays is opposite to that for the deviable  $\beta$ -uranium rays.

The emanating power of radium is increased more than 10,000 times by heating to dull redness. From the rate of leakage from excited radio-



activity, it is deduced that the speed of formation of ions by this is greater than by the direct radiation. The penetrating power of radium-excited radiation is independent of the substance in which it is produced. The decay of excited radioactivity has been found to be a function of the time of exposure. J. McC.

**Electrolysis of Molten Salts.** By RICHARD LORENZ (*Zeit. anorg. Chem.*, 1902, 31, 385—390. Compare Abstr., 1901, ii, 142).—The author corrects some misconceptions in connection with his work on this subject. J. McC.

**Conductivity of Mixtures of Electrolytes.** By BR. SABAT (*Zeit. physikal. Chem.*, 1902, 41, 224—231).—The author has determined the conductivity of mixtures of hydrochloric, nitric, and sulphuric acids, and finds, within certain concentration limits, a fair agreement with the values calculated by Barmwater's formulæ (Abstr., 1899, ii, 396). J. C. P.

**Relation between Current Intensity and Manifestation of Electrolysis.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1902, 135, 5—8).—Previous experiments are extended to cases in which the *E.M.F.* only slightly exceeds that necessary for the electrolysis of water. The element employed contained solutions of sodium hydroxide with the addition of a small quantity of pyrogallol, and of sodium chloride with the addition of a little hydrogen peroxide, and the *E.M.F.* was about 0.86 volt. With two such elements in a voltameter containing sulphurous acid, no electrolysis was observed under 760 mm. pressure, but the action was evident under 8 mm. On the addition of pyrogallol, the action was evident under the ordinary pressure. This is in accord with previous observation, as it had been found that in the first case the quantity of hydrogen which could be liberated, about 0.00001 mgm. per minute, would only be visible under reduced pressure. Electrolysis was apparent with one element under reduced pressure and on the addition of pyrogallol, and the rate of evolution is calculated to be 0.000003 mgm. per minute, a quantity only just on the limits of possible observation. L. M. J.

**Electromotive Behaviour of Hypochlorous and Chloric Acids.** By ERICH MÜLLER (*Zeit. Elektrochem.*, 1902, 8, 425—439).—The author has shown (Abstr., 1900, ii, 643) that when a solution of a chloride is electrolysed with gradually increasing applied *E.M.F.* (the anode being a point of smooth platinum and the cathode a hydrogen electrode), there are two changes of direction (at 1.3 and 1.9 volts) in the curve representing the current passing. The second change (at 1.9 volts) is not observed when the anode is platinised, and it is not so well marked when the electrolyte is acid as when it is alkaline. Measurements are made of the *E.M.F.* of cells consisting of a hydrogen electrode and of a smooth platinum electrode immersed in an acid or alkaline solution of hypochlorous acid, or of chloric acid. The results show that chloric acid gives a very much lower *E.M.F.* than hypochlorous acid of similar concentration. A solution of hypo-

chlorous acid of about normal strength gives an *E.M.F.* about 0.1 volt higher than a saturated solution of chlorine. The author considers that these observations are best explained as follows. The change occurring at the anode is  $\text{Cl}' + \text{OH}' = \text{HClO} + 2F$ . In presence of a platinised electrode, the hypochlorous acid is very rapidly decomposed, so that its concentration can never rise much above the value corresponding with the equilibrium  $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HClO} + \text{HCl}$ . The decomposition point observed at 1.3 volts corresponds with the establishment of this equilibrium. With a smooth platinum anode, the catalytic decomposition of hypochlorous acid is very much slower, and its concentration may therefore become considerably greater than that given by the equilibrium. The higher decomposition point would thus be due to the formation of a concentrated solution of hypochlorous acid at the anode. That a solution of hypochlorous acid does not give so high an *E.M.F.* may be due to the fact that the concentration in contact with the electrode is diminished by catalytic decomposition and electrolytic reduction to a lower value than it would have if the hypochlorous acid were being formed at the electrode. T. E.

**Accuracy of the Improved Voltmeter.** By THEODORE W. RICHARDS and GEORGE W. HEIMROD (*Zeit. physikal. Chem.*, 1902, 41, 302—330).—The authors previously (Abstr., 1900, ii, 256) recommended the insertion of a porous cell between the electrodes of the silver voltmeter, and further experiments show that this form of apparatus gives very uniform and trustworthy results. The weight of silver deposited on the platinum crucible is the same as that deposited in a voltmeter where the cathode is placed above the anode, and this weight is less than that obtained in any other form of voltmeter. The higher value obtained in most voltmeters is accounted for mainly by the formation at the anode of a complex silver ion such as  $\text{Ag}_3^+$ ; this ion would be readily decomposed on continued contact with the anode, giving the finely divided silver usually found there, but in so far as it is transferred to the cathode it would lead to an excessive increase in the cathode deposit. Nitrite is formed at the anode, but this has only a slight influence on the weight of the cathode deposit.

The correct value for the electrochemical equivalent of silver is estimated to be 0.0011175 mgm. per coulomb. The electrochemical equivalent of copper is 0.00032929 mgm. per coulomb; this leads to a value for the atomic weight of 63.601, agreeing closely with that found by purely chemical methods (63.604).

The term "coulometer" is proposed as a substitute for "voltmeter." J. C. P.

**Electrolysis of Silver Nitrate.** By ANATOLE LEDUC (*Compt. rend.*, 1902, 135, 23—25).—It is generally stated that silver nitrate becomes acid during electrolysis, but Rodger and Watson found that the acidity of a silver nitrate bath diminished. The apparent contradiction is due to a difference of condition; with platinum electrodes in a sufficiently concentrated solution, a brown solid containing a higher oxide of silver is formed with simultaneous formation of nitric acid, which, however, when a sufficient concentration is reached, reacts on the

compound with formation of oxygen. Similar results are obtained with soluble anodes and current of sufficient density, and the acidity of the bath therefore leads to a limiting value. The author finds that corrosion or solution of the cathode deposit does not take place, and the experiments also indicate that in a silver nitrate voltameter the polarisation *E.M.F.* is about 0.03 volt.

L. M. J.

**The Electrochemical Equivalent of Silver.** By ANATOLE LEDUC (*Compt. rend.*, 1902, 135, 237—240).—The author calls attention to the differences in the determinations of the electrochemical equivalent of silver which have been made, and discusses the causes of these. With a normal solution of silver nitrate at the ordinary temperature, if the anodic density is lower than 0.002 C.G.S. units, nitric acid is not formed at the anode in appreciable quantity. Under these conditions, the cathode deposit of silver is quite normal. If the anodic density is greater, the concentration lower, or the temperature higher, nitric acid is formed and disturbs the deposition of the silver at the cathode. When the current density is greater, the ill effect of the acid can be destroyed by adding silver oxide to the bath. If the proper conditions as to temperature, current density, acidity and basicity of the bath, and concentration be adhered to, it is possible to determine the electrochemical equivalent to 1/10000.

J. McC.

**Velocity of Ions in a Flame containing Salts.** By GEORGES MOREAU (*Compt. rend.*, 1902, 134, 1575—1577).—The conductivity of a flame containing a vaporised salt is of an electrolytic nature, and hence, from the conductivity, the velocity of the ions in the flame may be calculated. Two platinum plates were placed respectively in a pure flame and one containing the salt, the flames being in contact. The plate in the pure flame was charged positively, and from the current produced, the velocity of the negative ions was determined. It was found that in the case of various potassium and sodium salts the velocity of the negative ion at any concentration is independent of the radicle which should furnish it, indicating that one negative ion really exists for all these salts, and that its mobility is a function of the concentration. According to the view of Arrhenius, this ion is OH produced by hydrolysis of the vaporised salt, but the author postpones the discussion of this hypothesis.

L. M. J.

**Carbon Ions.** By JEAN BILLITZER (*Monatsh.*, 1902, 23, 502—511. Compare Coehn, *Abstr.*, 1901, ii, 539).—On electrolysis at 18° of an aqueous solution of silver acetylide or copper acetylide, or of a solution of acetylene in aqueous sodium hydroxide, the curve representing voltage and current intensity shows breaks at 0.75, 1.09, and 1.27 volts. The break at 1.27 is caused by depolarisation of the hydroxyl ions by acetylene liberated by hydrolysis, the discontinuity at 1.09 is due to the formation of oxygen ions, and that at 0.75 must represent the formation of carbon ions C<sub>2</sub>. With silver acetylide solution at 28° and 38°, the breaks representing the carbon ions are at 0.82 and at 0.87 respectively; with sodium acetylide at 36° and 60°, the break is at 0.86 and at 1.02 respectively.

From the figures obtained, the heat of formation of acetylene is calculated by Helmholtz's equation to be  $-49.5$  Cal., which agrees fairly closely with the value  $-53.2$  Cal., estimated directly.

With a solution of silver acetylide, an anode potential of  $0.9$  volt, and a platinum electrode with a surface of  $10$  sq. cm., the current intensity cannot be increased beyond  $0.0001$  ampere. After some weeks, small, silver crystals are observed on the cathode, and a slight, smooth, dark deposit on the anode. The anode deposit does not contain silver, leaves no residue when heated in a bunsen flame, is dissolved by chromic acid, and is undoubtedly carbon. G. Y.

**Electrolytic Phenomena at the Surface of Separation of Two Solvents.** By WALTHER NERNST and E. H. RIESENFELD (*Ann. Physik.*, 1902, [iv], 8, 600—608).—When a current passes through a U-tube containing a solution at the bottom and another solvent on both sides, electrolytic phenomena take place on account of the migration of the dissolved substance. The deduction is made that the electrolyte diffuses into the two solvents according to the distribution ratio and the ratio of the square root of the diffusion coefficients. The quantity of electrolyte which remains at the surface of separation depends only on the current passed through and on the difference of the transport numbers of the electrolyte in the two solvents.

This has been experimentally proved with potassium tri-iodide in water and water saturated with phenol. It has also been proved by experiments with potassium dichromate, ferric thiocyanate, and o-nitrophenol. With the latter, there is an increase of concentration at the anode and a decrease at the cathode, the change being easily recognised by the colour. With potassium tri-iodide, the increase of concentration takes place at the cathode. The method can be used to determine the transport number in one solvent if that in the other is known. J. McC.

**Transport Number of some Salts in Phenol.** By E. H. RIESENFELD (*Ann. Physik.*, 1902, [iv], 8, 609—615).—In order to test the method suggested in the preceding abstract for determining the transport number, the change of concentration of an aqueous solution over a phenol solution in a U-tube was determined when a current was passed through. The transport number is then found from the loss of anion at the cathode and the quantity of silver separated in an interposed voltameter. The transport number in phenol is independent of the concentration of the solution, of the duration of the electrolysis, and of the form and size of the vessel. The transport number for potassium (in potassium chloride, bromide, or iodide) in phenol is  $0.81$ ; for lithium (in lithium chloride) it is  $0.77$ . J. McC.

**Concentration Elements with Immiscible Solvents.** By E. H. RIESENFELD (*Ann. Physik.*, 1902, [iv], 8, 616—624).—When two immiscible solvents containing a common dissolved electrolyte are in contact, three equilibria have to be established: (1) that between the undissociated parts in the two solutions, (2) and (3) those between like ions in the two solutions. An *E.M.F.* is thus set up at the surface of separation which, however, cannot yet be measured. Nernst's

theory on this equilibrium enables the author to calculate the *E.M.F.* of a cell which contains a solution of the electrolyte in an immiscible solvent interposed between the two solutions of different concentrations. The formula developed is  $E.M.F. = 2nRT/m \cdot \log(c_1/c_2)$ , where  $n$  is the transport number in the interposed solvent,  $m$  the valency of the ion, and  $c_1$  and  $c_2$  are the concentrations. Experiments have been carried out with potassium chloride, potassium bromide, potassium iodide, and lithium chloride, the interposed solvent being phenol. The current flows from the concentrated solution to the dilute solution through the element. The values of the *E.M.F.* may be used to calculate the transport number and in this way the numbers found are : for potassium chloride, bromide, and iodide, 0.645, 0.643, and 0.646 respectively ; for lithium chloride, 0.574. In all cases, these are lower than the transport numbers already found (see preceding abstract). J. McC.

**Magnetism of Alloys of Iron and Silicon.** By AD. JOUVE (*Compt. rend.*, 1902, 134, 1577—1579).—The attraction of an electro-magnet on a constant mass of the alloy was determined, and a curve is given for attraction against composition. It is seen that two sudden changes occur at places corresponding with the compositions represented by  $\text{Fe}_2\text{Si}$  and  $\text{FeSi}$ , which compounds the author considers to be the only ones produced. The variation of the attraction further affords a method for the rapid determination of the percentage of silicon in the alloy. L. M. J.

**Thermal Properties of Carbon Dioxide and of Ethane.** By J. P. KUENEN and W. G. ROBSON (*Phil. Mag.*, 1902, [vi], 3, 622—630).—From examination of all the trustworthy data, the authors find that carbon dioxide obeys satisfactorily the law of corresponding states. The mean density of liquid and saturated vapour is, however, not a straight line but slightly convex towards the temperature axis. From the law of corresponding states, the vapour volumes below  $0^\circ$  are calculated and hence by means of the expression  $L = (V_v - V_e)T \cdot dp/dt$ , the latent heat of evaporation is obtained ; the value of the latter was found to decrease from 95.3 cal. at  $-65.7^\circ$  to 56.0 cal. at  $0^\circ$ . At the triple point  $-56.24^\circ$ , the value is 86.1 cal. ; the density of the solid is about 1.48, and the latent heat of sublimation is found to be about 129.9 cal., and hence the latent heat of fusion is 43.8 cal. At the boiling point, the latent heat of sublimation is about 121 cal. ; it hence increases with rise of temperature. In the case of ethane, the latent heat of evaporation was found to decrease from 111 cal. at  $-74.7^\circ$  to 45.7 cal. at  $22.9^\circ$ , the slope of the curve being considerably greater than in the case of carbon dioxide. L. M. J.

**Conductivity and Atomic Heat of the Metals.** By FRANZ STREINTZ (*Ann. Physik.*, 1902, [iv], 3, 847—853).—From the known electrical conductivities of metals at various temperatures, the author shows that in all cases the temperature coefficient is greater than  $1/273$ . In the group of metals with high atomic weight, the temperature coefficient increases with the atomic weight. This applies also to metals the atomic weight of which lies between 100 and 120 ; for

metals of lower atomic weight, it is only applicable to copper and zinc.

Metals of high atomic weight have a negative temperature coefficient of heat conductivity. The ratio of the two conductivities is only proportional to the absolute temperature for metals of medium atomic weight.

The temperature coefficient of the atomic heat is apparently connected with the temperature coefficient of the electrical conductivity, and the author draws the conclusion that for a metal of high atomic weight the smaller the displacement of the atoms compared with the distance between the atoms, the greater is the temperature coefficient of the electrical resistance. J. McC.

**Conductivity and Dielectric Constant of Solvents and Solutions and the Influence of Temperature to beyond the Critical Point on These.** By P. EVERSHEIM (*Ann. Physik.*, 1902, [iv], 8, 539—567).—The conductivity and dielectric constant of liquid sulphur dioxide has been determined at temperatures from 14.5° to 157.5°; both decrease as the temperature rises and immediately before the critical point the fall is very sudden, but there is no discontinuity. From the dielectric constants found it is shown that the Clausius and Mosotti formula does not lead to a constant value but is dependent on the absolute temperature. The addition of potassium chloride, potassium bromide, or rubidium iodide to the sulphur dioxide conditions a great increase in the conductivity. The conductivity of these solutions decreases with rising temperature, and shows a sharp fall near the critical point.

The dielectric constant of ethyl ether was determined and again it was found that the Clausius and Mosotti expression is dependent on the temperature. The conductivity of a solution of hydrogen chloride in ethyl ether decreases as the temperature rises, and the resistance becomes very great just at the critical point; the resistance has a minimum value at about -20°. The densities of ethyl ether and ethyl chloride at temperatures from 15° to 195° have also been determined. The dielectric constant of ethyl chloride and the conductivity of a solution of mercuric chloride in that solvent have been determined at various temperatures and the relationships are the same as those found for ethyl ether and its solution. J. McC.

**Molecular Attraction.** By J. E. MILLS (*J. Physical Chem.*, 1902, 6, 209—236).—The validity of the expression  $PV = RT$  for dissolved substances leads to the conclusion that the average translational energy of gaseous and liquid molecules at the same temperature must be equal. The internal latent heat is, therefore, solely spent in altering the distance of the molecules. Assuming that the attraction between the molecules varies inversely as the square of the distance, an expression is deduced for the energy necessary to produce an expansion of mass  $M$  from density  $d$  to density  $D$ ; this is  $M\mu c(\sqrt[3]{d} - \sqrt[3]{D})/\sqrt[3]{m}$ , where  $m$  is the weight of the molecule,  $\mu$  the attraction at unit distance, and  $c$  an unknown constant. Hence it follows that the ratio of the internal latent heat at two temperatures is equal to the ratio

of the values ( $\sqrt[3]{d} - \sqrt[3]{D}$ ) for these temperatures, assuming that  $\mu$  is constant, and this affords a test of the validity of the expression. In the twenty cases examined, the agreement is very satisfactory, but the ratios in many instances being near unity, the results are further tested by comparison of the difference between the two latent heats with that deduced by means of the expression. Only in the cases of water and ethyl alcohol is the difference greater than 5 calories, and in these compounds it is doubtful whether constancy of the number of molecules at different temperatures can be justly assumed. The values of the internal latent heat deduced from the author's expression are also compared and found to agree with those obtained by Crompton's formula,  $L_T = 2RT \log_e d/D$ . The author considers that these results afford evidence to prove that (1) molecular attraction varies inversely as the square of the distance, (2) the attraction constant is only slightly affected by temperature, (3) the attraction depends primarily on the chemical constitution of the molecule.

L. M. J.

**Thermodynamics and the Dissociation Theory for Binary Electrolytes.** By MAX PLANCK (*Zeit. physikal. Chem.*, 1902, 41, 212—223).—The conclusions which can be drawn from the laws of thermodynamics alone, as applied to the case of a binary electrolyte, are clearly distinguished from those which can be drawn with the addition of the dissociation hypothesis. In agreement with Jahn and Nernst, the author regards the dynamical methods of determining the degree of dissociation from the conductivity or from reaction velocities as inferior to the statical methods, that is, those depending on the determination of the osmotic pressure and allied quantities. The conductivity method of determining the degree of dissociation is based on the assumption that the mobility of the ions is independent of the concentration, and in support of this there is as yet no experimental evidence.

J. C. P.

**Outline of an Expanded Theory of Dilute Solutions.** By HANS JAHN (*Zeit. physikal. Chem.*, 1902, 41, 257—301).—As is well known, strong electrolytes do not obey Ostwald's law, and the question has arisen how far the ordinary methods of determining the degree of dissociation are valid in these cases. The abnormal behaviour of strong electrolytes may be due to some action between the ions and molecules of the solute. On this assumption, the author arrives thermodynamically at certain equations for the dissociation isotherm, the depression of the freezing point, the *E.M.F.* of concentration cells, &c. Thus, instead of the old form,  $n_1^2/(N - n_1) = K$ , for the dissociation isotherm, the author obtains the equation  $n_1^2/(N - n_1).e^l = k$ , where  $l = -aN/n + n_1(2a/n - b/n)$ ;  $a$  and  $b$  are functions of the pressure, the temperature, and the composition of solute and solvent,  $a$  expressing the action between the ions and the undissociated molecules,  $b$  the action between the ions themselves. An action of the ions on the undissociated molecules would be possible when the latter had a dielectric constant differing from that of the surrounding medium. On *a priori* grounds,  $b$  is assumed to be small, and the abnormal behaviour of strong electrolytes is thus attributed to the action of the free ions on the undis-

sociated molecules. This introduces a simplification in the author's equations, and their applicability and consistency are tested for potassium and sodium chlorides. In these cases, it is shown that  $K$  of the equation quoted above is satisfactorily constant, and has the same value whether the degree of dissociation is obtained from the freezing point or from a concentration cell. The freezing point data used are those of Abegg and Loomis, and the author himself has measured the *E.M.F.* of suitable concentration cells; from these experimental data, the degree of dissociation is calculated by the author's own equations.

The conductivity can be accepted as a measure of the dissociation only in very dilute solutions, since apparently the mobilities of the ions change with the concentration.

J. C. P.

**Molecular Condition of Potassium Iodide [dissolved] in Phenol.** By E. H. RIESENFELD (*Zeit. physikal. Chem.*, 1902, 41, 346—352).—From partition and conductivity experiments, it appears that potassium iodide is strongly dissociated in phenol which is saturated with water; the mobility of the ions in this medium is about one-fifth of that in pure water.

The molecular weight of potassium iodide in anhydrous phenol (determined cryoscopically) is normal, and a study of the conductivity of the solutions shows that the dissociation is but slight. When water is added to a solution of potassium iodide in anhydrous phenol, the resistance diminishes almost in proportion to the amount of water added.

J. C. P.

**Behaviour of Succinic and Phthalic Anhydrides towards Water.** By E. VAN DE STADT (*Zeit. physikal. Chem.*, 1902, 41, 353—369).—The complete freezing point curves for mixtures of (1) succinic anhydride and water, (2) phthalic anhydride and water, have been determined. In each case, there is one well-marked rounded summit, corresponding with the formation of the acid. The eutectic points on either side are only very slightly below the freezing points of anhydride and water, owing to the slight solubility of either acid in water at 0°, and in the anhydride at its melting point. The author's results are therefore in conflict with Bancroft's view (*Abstr.*, 1899, ii, 411) that phthalic acid and anhydride form a continuous series of mixed crystals. The fact that the summits of the freezing point curves are rounded shows that the acids in the liquid condition are partly dissociated; accurate determinations, therefore, of the freezing points can be made only in closed vessels. At low temperatures, the anhydrides dissolve as such in water (compare van de Stadt, *Abstr.*, 1900, i, 200), and are hydrated very slowly. The rapidity of hydration increases with the temperature, and above 100° the anhydride in contact with water is instantly converted into the corresponding acid. Owing to the rapid establishment of equilibrium between water, anhydride, and acid in the liquid phase, the rate of heating has no effect on the value obtained for the melting point of the acids or their anhydride mixtures, provided, of course, water vapour does not escape. This also is in conflict with Bancroft's observations.

J. C. P.



**Study of Diffusion.** By J. THOVERT (*Ann. Chim. Phys.*, 1902, [vii], 26, 366—432).—This contains a mathematical treatment of the phenomenon of the diffusion of liquids and solutions, and is not suitable for abstraction. G. T. M.

**The Equation of Fluids.** By PHILIPPE A. GUYE and L. FRIDERICH (*Arch. Sci. Phys. Nat.*, 1902, 13, 559—568).—The values of  $a$  and  $b$  in van der Waals' equation have been previously published for a large number of compounds at the critical state (Abstr., 1900, ii, 709). For a liquid sufficiently removed from the critical condition, the value of  $p$  in the equation is negligible compared with  $a/v^2$ , and the equation reduces to  $a/v^2 = RT/(v - b)$ , and by elimination of  $b$  from two such equations  $a = R(T_2 v_2^2 - T_1 v_1^2)/(v_2 - v_1)$ . The value of  $a$  can also be obtained from the equation  $a/v^2 = RT/(v - b)$ , or from the original van der Waals' equation by differentiation. For the vapour phase, the values of  $a$  and  $b$  are obtained by the combination of van der Waals' equation with that of Ramsay and Young,  $p = \beta T - a$  ( $v = \text{constant}$ ). The values for  $a$  and  $b$  in the liquid and vapour phases were thus determined in the case of isopentane and found to differ considerably. Thus at  $30^\circ$  for liquid isopentane,  $a \times 10^{-6} = 11.54$ ,  $b = 88.2$ ; whilst for the vapour,  $a \times 10^{-6} = 40.63$ ,  $b = 415$ , the values at the critical state being 18.33 and 143.6. L. M. J.

**Vapour Pressures in the System: Water-Acetone-Phenol.** III. By FRANZ A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1902, 41, 331—345. Compare this vol., ii, 243, 380).—The composition of the systems, which at various temperatures have a vapour pressure of (1) 380 mm., (2) 760 mm. has been determined, and the results are represented graphically on triangles. The conditions are then deduced under which a three phase system consisting of two liquids and a vapour, the pressure of the latter being 380 mm., can exist.

When water is added to a phenol-acetone mixture, it depends on the composition of the latter whether its boiling point under 760 mm. will be raised or lowered (compare Schreinemakers, Abstr., 1901, ii, 445, 641). The limiting binary mixture in this case contains 34.8 per cent. of phenol and 65.2 per cent. of acetone. The boiling point of a mixture containing more phenol will be at first lowered by the addition of water, that of a mixture with less phenol will be continuously raised. Addition of phenol to aqueous acetone first produces depression of the boiling point when the mixture contains less than about 5 per cent. of acetone: the boiling point of mixtures with more than 5 per cent. of acetone is continuously raised by the addition of phenol. The addition of acetone to water-phenol mixtures (whatever their composition) produces a depression of the boiling point. J. C. P.

**Observations on Mixtures with Maximum or Minimum Vapour Pressure.** By J. P. KUENEN and W. G. ROBSON (*Phil. Mag.*, 1902, [vi], 4, 116—132. Compare Abstr., 1901, ii, 146).—The simultaneous occurrence of a maximum vapour pressure with a minimum critical temperature or of a minimum vapour pressure with a maximum critical temperature is a consequence of van der Waals' theory, pro-

vided that there is no association of the liquids. A mixture of propyl alcohol and water containing .25 per cent. of water has a maximum vapour pressure which it retains up to the critical temperature, and the critical temperature shows no minimum. This abnormality is traced to the association of the water molecules. A mixture containing acetone and chloroform has a minimum vapour pressure which moves as the temperature rises and disappears at the critical temperature, which itself exhibits no maximum. The vapour pressures of mixtures of carbon dioxide and ethane were determined at temperatures below  $0^{\circ}$ ; this mixture has a maximum vapour pressure and a minimum critical temperature, but no separation into two liquid phases was brought about by lowering the temperature. The authors also discuss the condensation of various mixtures of carbon dioxide and ethane at different temperatures, solidification, and the heats of evaporation.

J. McC.

**Studies in Vapour Composition. II.** By H. R. CARVETH (*J. physical Chem.*, 1902, 6, 237—256).—A paper in which the author discusses methods for the determination of the boiling point; this and other physical constants are frequently taken in systems for which all the equilibrium factors are not specified or considered. It is shown that superheating may be avoided and a constant boiling point obtained by employing the vapour as the source of heat even when the vapour itself is superheated, as changes in its temperature have practically no effect on the boiling point. By passing vapour A into liquid B, the boiling point changes in a continuous manner from that of A to that of B, and boiling point curves may be readily investigated in this way, which is especially convenient for the determination of maxima or minima. Dephlegmation and continuous distillation are also briefly discussed.

L. M. J.

**Solubility of Carbon Monoxide in Binary Organic Mixtures.** By FREDERICK WILLIAM SKIRROW (*Zeit. physikal. Chem.*, 1902, 41, 139—160).—The method employed was, with slight modifications, that of Just (*Abstr.*, 1901, ii, 439). Except where analysis was possible, the composition of a mixture of two liquids was obtained from the index of refraction by interpolation, the empirical curve giving the relation of these two quantities being already known.

When one of the components of the mixture is very volatile, and the other slightly volatile, as in mixtures of benzene, toluene, acetone, or acetic acid with aniline or nitrobenzene, the solubility is mainly additive, the solubility curves being slightly convex towards the composition axis. The same holds for solutions of naphthalene, phenanthrene, and  $\alpha$ - and  $\beta$ -naphthol in benzene, toluene, or acetone.

In the case of two easily volatile liquids, it was thought that there might be some connection between the vapour pressure curve and the carbon monoxide solubility curve. The vapour pressure curve for mixtures of acetone and chloroform shows a minimum, but the solubility curve exhibits no special feature. Neither in cases where there is a maximum in the vapour pressure curve (acetone-carbon disulphide, benzene-ethyl alcohol, chloroform-methyl alcohol) was any peculiarity

discoverable. On the other hand, a connection was found between the surface tension and carbon monoxide solubility curves of certain mixtures. Where the surface tension curve exhibits a minimum, as in the cases acetic acid and benzene, acetic acid and toluene, acetic acid and chloroform, carbon disulphide and ethylene dichloride (compare Whatmough, this vol., ii, 125), the carbon monoxide solubility curve shows a maximum.

J. C. P.

**Cause of the Influence of Positive and Negative Catalysers on the Velocity of Hydration in some Inorganic Reactions.** By PAUL ROHLAND (*Zeit. anorg. Chem.*, 1902, **31**, 437—444. Compare Abstr., 1899, ii, 596; 1901, ii, 18).—The author has collected the results previously obtained on the influence of certain salts on the velocity of hydration of calcium sulphate, calcium oxide, and Portland cement. The velocity of hydration depends on the solution pressure of the substance in the solution under examination. If the calcium sulphate is more soluble in a solution of a particular salt than in water, the velocity of hydration is increased, but if it is less soluble the hydration is retarded. The cause of this may be the formation of complex ions.

J. McC.

**Formation of Colloidal "Bubbles" from Heptylamine Soaps and Water. I.** By FRIEDRICH KRAFFT (*Zeit. physiol. Chem.*, 1902, **35**, 364—375. Compare Abstr., 1896, ii, 468, and Donnan, Abstr., 1900, ii, 201).—A *résumé* of early work on formation of emulsions and froth. The colloidal nature of a sodium soap increases with the molecular weight of the acid molecule. Similarly, the colloidal nature of the hydrochloride of organic amines increases with the molecular weight of the base. It is now shown that the formation of membranes is exhibited to an extraordinary degree by soaps formed from a base and an acid both of high molecular weight: for example, heptylamine oleate.

J. J. S.

**Formation of Colloidal "Bubbles" from Heptylamine Soaps and Water. II.** By FRIEDRICH KRAFFT and R. FUNCKE (*Zeit. physiol. Chem.*, 1902, **35**, 376—385. Compare preceding abstract).—Heptylamine soaps are readily prepared by bringing their constituents together in a liquid state and allowing the mixture to solidify. They form crystalline plates and melt at temperatures slightly lower than those of the acids from which they are derived, thus *heptylamine oleate* melts at 13·8° and the acid at 14°; the *elaidate* at 45° and the acid at 45°; the *erucate* at 21·5° and the acid at 33°; the *brassidate* at 44·5° and the acid at 60°.

These soaps are not so readily dissociated by water as the sodium soaps of the same acids. The formation of colloidal bubbles may readily be observed at the ordinary temperature when heptylamine oleate or erucate is brought into contact with water. Although molten heptylamine soaps have no action on polarised light, the colloidal emulsions are strongly doubly refractive. The heptylamine soaps of higher melting point do not exhibit swelling (Quellung) with cold water, but with tepid water show the same phenomena as the

soaps of lower melting point. As the temperature falls, crystals separate, and often both crystals and "bubbles" can be observed in the same liquid (compare Abstr., 1901, i, 63). The colloidal bubbles are readily coloured by methylene-blue, &c.

J. J. S.

**General Numerical Connection between the Atomic Weights.** By J. H. VINCENT (*Phil. Mag.*, 1902, [vi], 4, 103—115).—The author gives an historical account of the numerical connections which have been deduced by Mills, Stoney, and Carnelley. The atomic weight is calculated from the formula  $W = (n + 2)^{1.21}$ , where  $n$  is the order on a list of atomic weights arranged in ascending magnitude. The mean percentage difference between the values found in this way and the determined atomic weights ( $H=1$ ) is 1.6. The formula gives results for known elements for values of  $n$  from 3 to 60. For the other elements, the formula is used in the form  $W = N^{1.21}$ , and from the values obtained it is clear that there are blanks in the list to be filled up by elements yet to be discovered. The applicability of this formula indicates that the list of atomic weights starts abruptly at hydrogen but has no end.

J. McC.

**The Ratios of the Atomic Weights.** By ARTHUR MARSHALL (*Chem. Zeit.*, 1902, 26, 663—664).—The author discusses the probability of the atomic weights being whole numbers. It is pointed out that when the atomic weights of certain series of elements are multiplied by an arbitrary factor, a ratio in whole numbers is obtained; thus, when the atomic weights of chlorine, bromine, silver, and iodine are multiplied by 2.53868, the ratio obtained is 90:203:274:322; for the alkali metals (including ammonium), the factor is 1.004, whilst for the metals vanadium, chromium, manganese, iron, nickel, cobalt, copper, and zinc, the factor is 1.0551. The theoretical significance of these regularities is not discussed.

J. McC.

**Apparatus for Studying Contact Reactions. Use of the Platinum Spiral.** By J. AUGUSTE TRILLAT (*Bull. Soc. Chim.*, 1902, [iii], 27, 797—803).—The author gives a description and illustration of an apparatus for studying oxidation phenomena induced by a red hot platinum spiral. The platinum spiral is enclosed in a narrow glass tube through which the vapour of the substance to be oxidised is passed along with air, and from which an outlet tube passes into a flask in which the products of oxidation can be collected. The spiral can be raised to incandescence by means of an electric current; in some cases, it is only necessary to use the current for the initial heating, the heat evolved on oxidation being then sufficient to maintain the spiral at a red heat. The tube containing the platinum spiral is surrounded by a water condenser to prevent the re-decomposition of the products of oxidation.

A. F.

## Inorganic Chemistry.

**Intensifying ("Activirende") Action of Reducing Agents, Colloidal Noble Metals, Alkaloids, and other Basic Substances on Oxidising Agents.** By EDUARD SCHAEER (*Annalen*, 1902, 323, 32—82).—The intensifying action of sulphurous acid, hydrogen peroxide, colloidal gold and platinum, alkaloids and insoluble carbonates on certain oxidising agents has been studied, using the oxidisable substances potassium iodide, guaiacum, indigo-carmin pyrogallol, guaiacol, *p*-phenylenediamine, and aloin as indicators.

A description of the experiments made on cupric salts has already been published (this vol., ii, 140).

Hydrogen peroxide, like sulphurous acid (Abstr., 1901, ii, 603), intensifies the oxidising action of ferric salts on indigo, and, in addition, promotes the oxidation of guaiacum, potassium iodide, *p*-phenylenediamine, and guaiacol. Colloidal platinum, although not inducing any action on indigo, renders the oxidising agent more active towards the other oxidisable substances.

Sulphurous acid does not intensify the action of mercuric chloride, and hydrogen peroxide does so only in the case of aloin. Colloidal platinum induces the oxidation of guaiacum and pyrogallol by this reagent, and both this metal and colloidal gold promote the development of the guaiacol coloration. Pyrogallol is oxidised both by mercuric chloride and ferric salts in the presence of insoluble carbonates and alkaloids. Silver nitrate oxidises indigo and aloin in the presence of hydrogen peroxide, whilst the guaiacum and guaiacol colorations are developed in the presence of the colloidal noble metals.

Hydrogen peroxide intensifies the action of chromic acid on all the oxidisable substances under examination (compare Bach, this vol., ii, 251). Sulphurous acid promotes the oxidation of indigo, guaiacum, and aloin, whilst colloidal gold and platinum render the oxidising agent more active towards pyrogallol, *p*-phenylenediamine, and potassium iodide.

Hydrogen peroxide intensifies the action of hypochlorous acid on *p*-phenylenediamine; the colloidal metals promote the oxidation of guaiacum and aloin by this acid.

Chloric acid and the chlorates are rendered more generally active by sulphurous acid, but are not affected by hydrogen peroxide or the colloidal metals. Sulphurous acid has a less marked effect on bromic acid and the bromates; pyrogallol and *p*-phenylenediamine are attacked by these reagents in the presence of the colloidal metals, which also induce a slight oxidation of aloin.

Iodates oxidise indigo, pyrogallol, *p*-phenylenediamine, and guaiacol under the influence of sulphurous acid, hydrogen peroxide promotes the oxidation of pyrogallol and *p*-phenylenediamine; this effect is likewise produced by colloidal platinum, which also intensifies the action of the oxidising agent on guaiacol and aloin.

Nitric acid and the nitrates readily oxidise indigo and guaiacum

under the influence of sulphurous acid; hydrogen peroxide promotes the decomposition of indigo and potassium iodide, whilst the action on pyrogallol, *p*-phenylenediamine, guaiacol, and the iodide is intensified by the presence of colloidal platinum. Permanganates act more energetically on potassium iodide and *p*-phenylenediamine in the presence of hydrogen peroxide; sulphurous acid induces the oxidation of indigo, whilst guaiacum and *p*-phenylenediamine are oxidised under the influence of colloidal platinum, aloin being also affected by colloidal gold.

Benzoic peroxide is rendered more active towards indigo, guaiacum, and guaiacol by the presence of sulphurous acid; hydrogen peroxide promotes the oxidation of indigo, especially in warm solutions, it also produces a similar effect in the case of *p*-phenylenediamine. Colloidal platinum also influences the oxidation of indigo in warm solutions, and causes the development of a faint coloration with aloin.

Quinone is rendered more active by hydrogen peroxide and colloidal platinum, the first agent promotes the oxidation of indigo, potassium iodide, and guaiacol, whilst the second intensifies the action on guaiacum, pyrogallol, and aloin. The last of these substances and leucaniline are also oxidised by quinone in the presence of sulphurous acid or colloidal gold.

G. T. M.

**Crystallised Hydrogen Peroxide.** By WILHELM STAEDEL (*Zeit. angew. Chem.*, 1902, 15, 642—643).—When a concentrated solution of hydrogen peroxide is cooled, it solidifies and the crystals melt at  $-2^{\circ}$ . A 90—95 per cent. solution remains liquid at  $-20^{\circ}$ , but solidifies in a freezing mixture of ether and carbon dioxide. The eutectic point lies between  $-20^{\circ}$  and  $-23^{\circ}$ . The crystals, which are anhydrous, are colourless and prismatic. The best method of obtaining anhydrous hydrogen peroxide is by this freezing out process. When a trace of platinum sponge or manganese dioxide is thrown on to the anhydrous preparation, an explosive decomposition takes place; a mixture of powdered carbon or magnesium with a trace of manganese dioxide inflames when dropped on to it.

When a 90—95 per cent. solution of hydrogen peroxide is added to a concentrated solution of cadmium chloride, silky crystals separate which contain 23 per cent. of hydrogen peroxide.

J. McC.

**Preparation of Sulphuryl Chloride.** ALFRED WOHL & OTTO RUFF (D.R.-P. 129862).—The transformation of chlorosulphonic acid into sulphuric acid and sulphuryl chloride in molecular proportion is readily effected by boiling the compound with mercury or mercuric sulphate. If the apparatus is fitted with a reflux condenser at  $70^{\circ}$ , the sulphuryl chloride distils over in quantitative yield. The process is continuous and other metallic salts, such as those of tin and antimony, may be employed as catalysts; sulphur dichloride and iodine monochloride also produce the same effect.

G. T. M.

**The Lead Chamber Process in the Light of Physico-chemical Theories.** By E. HAAGN (*Zeit. angew. Chem.*, 1902, 15, 583—585).—The author believes that the lead chamber process can best be explained by physico-chemical theories on the assumption that

nitrosylsulphuric acid is formed as an intermediary product. Since this substance has a very low vapour tension, it is removed from the reaction mixture and thus the reaction is accelerated. J. McC.

**Theory of the Lead Chamber Process.** By GEORG LUNGE (*Zeit. angew. Chem.*, 1902, 15, 581—583. Compare this vol., ii, 315).—A reply to Th. Meyer (*Zeit. angew. Chem.*, 1901, 14, 1245; 1902, 15, 278) and Riedel (this vol., ii, 450). J. McC.

**Selenium. II.** By JULIUS MEYER (*Zeit. anorg. Chem.*, 1902, 31, 391—400).—A full account of the determination of the atomic weight of selenium (see this vol., ii, 392). Selenium can be completely reduced and separated in the elementary condition from an acid solution of a selenite by hydrazine. J. McC.

**Direct Hydrogenation of Nitrogen Oxides by Contact Action.** By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1902, 135, 278—281).—When a mixture of nitrous oxide and hydrogen is passed over reduced nickel, a reaction takes place at the ordinary temperature with a large development of heat, and in presence of excess of hydrogen the oxide is completely reduced without any formation of ammonia. If the oxide is in excess, the front part of the metal becomes incandescent, higher nitrogen oxides appear in the cooler part of the tube, and a little ammonia is formed. Reduced copper behaves in the same way as nickel, but reduction does not take place below 180°. Mixtures of nitric oxide with excess of hydrogen are not reduced by nickel below 180°, but above this temperature water, ammonia, and nitrogen are formed. With excess of nitric oxide, the metal becomes incandescent. Copper behaves in the same way as nickel. With nitrogen peroxide and hydrogen, the phenomena are similar, but if the proportion of the peroxide is increased, ammonium nitrite and nitrate are formed as well as ammonia, and when the proportion exceeds a certain limit the metal becomes incandescent and an explosion usually occurs. Mixtures of nitric acid vapour and hydrogen are reduced in a similar manner.

C. H. B.

**Reactions in the Formation of Calcium Carbide.** By G. GIN (*Zeit. Elektrochem.*, 1902, 8, 397).—Free oxygen is found in the gases formed in the hottest portions of a calcium carbide furnace, whilst calcium vapour is found in cooler portions of the furnace. The author suggests that these substances may be formed by the reactions  $2\text{CaO} + 4\text{C} = 2\text{CaC}_2 + \text{O}_2$  and  $\text{CaC}_2 + 2\text{CaO} = 3\text{Ca} + 2\text{CO}$ , the temperature in the hottest zones of the furnace being higher than the dissociation temperature of carbon monoxide. T. E.

**Separation of Beryllium.** By GRÉGOIRE N. WYROUBOFF (*Bull. Soc. Chim.*, 1902, [iii], 27, 733—734).—For the purpose of separating beryllium from aluminium and iron, which generally accompany it in minerals, the author takes advantage of the fact that beryllium oxalate is very sparingly soluble, whereas the oxalates of aluminium and of iron are comparatively soluble in water. A. F.

**Properties and Constitution of Zinc Peroxides.** By ROBERT DE FORCRAND (*Compt. rend.*, 1902, 135, 103—106).—The zinc peroxides  $\text{Zn}_3\text{O}_5 \cdot 2\text{H}_2\text{O}$ ,  $\text{Zn}_3\text{O}_5 \cdot 3\text{H}_2\text{O}$ ,  $\text{Zn}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ , and  $2\text{ZnO}_2 \cdot 5\text{H}_2\text{O}$  (this vol., ii, 322) are stable in moist or dry air with the exception of the last, which at the ordinary temperature gradually changes into  $\text{Zn}_3\text{O}_5 \cdot 2\text{H}_2\text{O}$ . At  $100^\circ$ , the compound  $\text{Zn}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$  is gradually converted into  $\text{Zn}_3\text{O}_5 \cdot 3\text{H}_2\text{O}$ , but both the hydrates of the oxide  $\text{Zn}_3\text{O}_5$  are stable at this temperature. The compound  $\text{Zn}_3\text{O}_5 \cdot 3\text{H}_2\text{O}$  at  $190^\circ$  and the compound  $\text{Zn}_3\text{O}_5 \cdot 2\text{H}_2\text{O}$  at  $210^\circ$  suddenly lose water and oxygen and are converted into the monoxide. All of them dissolve in dilute sulphuric acid without liberation of oxygen, yielding a solution which behaves like a mixture of zinc sulphate and hydrogen peroxide. The thermal disturbances at  $15^\circ$  are :

$\text{Zn}_3\text{O}_5 \cdot 2\text{H}_2\text{O}$ sol. + $3\text{H}_2\text{SO}_4$ diss. develops	+ $16 \cdot 04 \times 3$ Cal.
$\text{Zn}_3\text{O}_5 \cdot 3\text{H}_2\text{O}$ „ + $3\text{H}_2\text{SO}_4$ „ „	+ $15 \cdot 49 \times 3$ „
$\text{Zn}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ „ + $4\text{H}_2\text{SO}_4$ „ „	+ $14 \cdot 86 \times 4$ „
$\text{ZnO}_2 \cdot 2\text{H}_2\text{O}$ „ + $\text{H}_2\text{SO}_4$ „ „	+ $14 \cdot 86$

If the compounds are regarded as true peroxides, all their heats of formation are largely endothermic, which scarcely agrees with their marked stability, but if they are compounds of zinc oxide with hydrogen peroxide, their heats of formation in the solid state from zinc oxide and liquid hydrogen peroxide are  $\text{Zn}_3\text{O}_5 \cdot 2\text{H}_2\text{O}_2$  sol. +  $12 \cdot 29 \times 2$  or +  $8 \cdot 19 \times 3$ ;  $\text{Zn}_3\text{O}_5 \cdot 2\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$  +  $12 \cdot 24 \times 2$  or +  $8 \cdot 16 \times 3$ ;  $\text{Zn}_4\text{O}_7 \cdot 3\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$  +  $11 \cdot 96 \times 3$  or +  $8 \cdot 97 \times 4$ , and  $\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}_2$  +  $4 \cdot 87$ . It is noteworthy that all the compounds contain at least as many mols. of water as there are atoms of active oxygen. C. H. B.

**Precipitation of the Chlorides and Bromides of Cadmium, Mercury, and Tin by Sulphuric Acid.** By GEORGES VIARD (*Compt. rend.*, 1902, 135, 242—244).—Cadmium chloride can be almost completely precipitated by adding an excess of sulphuric acid to the aqueous solution. The chloride is slightly attacked by the acid in the cold. Depending on the amount of sulphuric acid used, the cadmium chloride separates as dihydrate or monohydrate.

Cadmium bromide is precipitated in the anhydrous form by an excess of sulphuric acid; it is not attacked in the cold by the acid.

Mercuric chloride and bromide and stannous chloride and bromide are precipitated by an excess of sulphuric acid. J. McC.

**Toning Solutions containing Lead Thionates.** By AUGUSTE LUMIÈRE and LOUIS LUMIÈRE and ALPHONSE SEYEWETZ (*Bull. Soc. Chim.*, 1902, [iii], 27, 792—797. Compare this vol., ii, 319).—The authors find that a toning-fixing solution of lead pentathionate and sodium thiosulphate yields results comparable with those obtained with a gold solution. On adding a quantity of gold equal to that contained in the ordinary toning-fixing solution, the tones obtained with a chlorocitrate paper are blacker and fresher than with the ordinary solution. Sulphur forms part of the toned image.

The authors have also tried other salts of lead, especially the various thionates, but the best results are given by the pentathionate. The solutions are, however, unstable and in course of time give a deposit



which appears to consist of sulphur, lead thiosulphate, and lead dithionate.  
A. F.

**Thallic Alum.** By AUGUSTO PICCINI and V. FORTINI (*Zeit. anorg. Chem.*, 1902, 31, 451—453. Compare Locke, this vol., ii, 497).—From thallic sulphate, the following double salts have been prepared:  $\text{Ti}_2(\text{SO}_4)_3 \cdot \text{R}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$  where  $\text{R} = \text{NH}_4$ , K, and Rb. The rubidium salt very easily loses water. Since indium ammonium alum passes at  $36^\circ$  into a double salt with 8 mols. of water, it seems probable that at some lower temperature the above thallic salts in contact with water would be transformed into the alums. Mixed crystals of ammonium alum with some of the aluminium replaced by thallium have been obtained. On sowing a supersaturated solution of ammonium alum with ammonium thallic sulphate, crystals of  $\text{Al}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$  separate. Hence the octahydrated form of the double sulphates appears to be common to the salts derived from the three elements of the aluminium family, the stability of the compounds increasing with the atomic weight of the metal.

J. McC.

**Cuprous Compounds. II.** By GUIDO BODLANDER and O. STORBECK (*Zeit. anorg. Chem.*, 1902, 31, 458—476. Compare this vol., ii, 502).—In attempting to determine the solubility of cuprous bromide it has been found that in water it partially decomposes into cupric bromide and copper. From the equilibrium relationships between cuprous ions, cupric ions, and metallic copper, it has been proved that the cuprous ion is monatomic. Cuprous bromide is easily soluble in a solution of potassium bromide; in a dilute solution of a bromide, the complex ion  $\text{CuBr}_2'$  is present, whilst in more concentrated solution the complex ion is  $\text{CuBr}_3''$ . The discharge potential of cuprous ions is  $-0.454$  volt.

The equilibrium relationships between cuprous iodide, cupric iodide, and iodine show that reaction occurs according to the equation:  $2\text{Cu}^{++} + 2\text{I}' = 2\text{Cu}^+ + \text{I}_2$ .

The solubility products of the cuprous haloids are:  $\text{CuCl}$ ,  $1.2 \times 10^{-6}$ ;  $\text{CuBr}$ ,  $4.15 \times 10^{-8}$ ; and  $\text{CuI}$ ,  $5.06 \times 10^{-12}$ . This is in agreement with Bodländer's rule (*Abstr.*, 1898, ii, 554) that the solubility decreases with diminishing discharge potential of the ions. In confirmation of Abegg and Bodländer's rule (*Abstr.*, 1899, ii, 542), it is found that the tendency towards the formation of complex ions increases as the decomposition tension or electro-affinity diminishes. Of the complex ions of the type  $\text{CuX}_2'$ , that containing iodine is the most stable and that with chlorine the least.

J. McC.

**Anhydrous Ammonio-cupric Chlorides: Cuprammonio-radicles.** By ALBERT BOUZAT (*Compt. rend.*, 1902, 135, 292—295).—The compound  $\text{CuCl}_2 \cdot 6\text{NH}_3$  is obtained by the action of liquefied ammonia on cupric chloride previously saturated with ammonia gas. It is a pale blue solid insoluble in liquefied ammonia, but soluble in water. It gradually dissociates, yielding the compound  $\text{CuCl}_2 \cdot 4\text{NH}_3$ , which has not previously been isolated, and its dissociation pressure is equal to atmospheric

pressure at about  $90^{\circ}$ . The compound  $\text{CuCl}_2 \cdot 4\text{NH}_3$  also readily dissociates, yielding the compound  $\text{CuCl}_2 \cdot 2\text{NH}_3$ , the dissociation pressure being equal to that of the atmosphere at about  $140^{\circ}$ . The heats of formation were determined by dissolving the compounds in (a) excess of ammonia solution, (b) excess of acid.

$\text{CuCl}_2 \text{ sol.} + 2\text{NH}_3 \text{ gas} = \text{CuCl}_2 \cdot 2\text{NH}_3 \text{ sol.}$  develops +45.5 Cal.

$\text{CuCl}_2 \text{ ,,} + 4\text{NH}_3 \text{ ,,} = \text{CuCl}_2 \cdot 4\text{NH}_3 \text{ ,,}$  +72.06 "

$\text{CuCl}_2 \text{ ,,} + 6\text{NH}_3 \text{ ,,} = \text{CuCl}_2 \cdot 6\text{NH}_3 \text{ ,,}$  +94.3 "

The heats of formation diminish and the dissociation pressure increases with an increase in the proportion of ammonia, and the value of the ratio  $Q/T$ , where  $T$  is the absolute temperature of dissociation at atmospheric pressure and  $Q$  is the heat of combination per mol. of ammonia, agrees with that found by Matignon in the case of other ammonio-chlorides.

$\text{Cu sol.} + 2\text{NH}_3 \text{ gas} + 2\text{HCl gas} = \text{Cu}(\text{NH}_3)_2\text{Cl}_2 \text{ sol.} + \text{H}_2 \text{ gas}$  develops +52.9 Cal.

$\text{Cu sol.} + 4\text{NH}_3 \text{ gas} + 2\text{HCl gas} = \text{Cu}(\text{NH}_3)_4\text{Cl}_2 \text{ sol.} + \text{H}_2 \text{ gas}$  develops +79.5 Cal.

$\text{Cu sol.} + 6\text{NH}_3 \text{ gas} + 2\text{HCl gas} = \text{Cu}(\text{NH}_3)_6\text{Cl}_2 \text{ sol.} + \text{H}_2 \text{ gas}$  develops +101.8 Cal.

C. H. B.

[Density of Cuprous Iodide.] A Correction. By WALTÈRE SPRING (*Rec. trav. chim.*, 1902, 21, 294. Compare Abstr., 1901, ii, 451).—The molecular volume of cuprous iodide is not 34.73 but 32.72. The mol. volume, 33.61, is rather greater than that derived from the sum of the elements, namely, 32.72, but much smaller than 43.08 which is given by the density obtained by Schiff. The formation of cuprous iodide, therefore, probably takes place with expansion, but not to the extent of justifying any definite conclusion with regard to the decomposition of the substance by compression.

A. F.

Pasty Condition assumed by Aluminium in the Neighbourhood of its Melting Point, and the Application of this Property to the Division of the Metal. By ALBERT GRANGER (*Bull. Soc. Chim.*, 1902, [iii], 27, 789—790).—When aluminium is heated to a temperature of about  $600^{\circ}$ , its tenacity and hardness become greatly modified, the metal assumes a grained structure, and can be easily broken. On heating to a still higher temperature, the metal can be cut with a knife or even crushed in a mortar.

A. F.

Dialysis Experiments with Metallic Hydroxides and Sulphides. By W. HERZ (*Zeit. anorg. Chem.*, 1902, 31, 454—457).—When an alkaline solution of aluminium, lead, or stannous hydroxide is placed in a dialyser, no precipitate is formed on the parchment and the metallic hydroxide easily passes through. With similar solutions of beryllium and zinc hydroxides, the colloidal substance does not diffuse so readily and there is a precipitation of the hydroxide on the membrane; with chromium hydroxide, there is no diffusion. This is in agreement with Hantzsch's view (this vol., ii, 395) that aluminium, lead, and stannous hydroxides are acids, beryllium and zinc hydroxides are weak acids, and chromium hydroxide has no acid properties.

When the brown solution obtained by dissolving nickel sulphide in ammonium sulphide is subjected to dialysis, the nickel partially diffuses but there is a large deposit of nickel sulphide on the membrane. This shows that the solution is not a colloidal one in the ordinarily accepted interpretation of that term. J. McC.

**Constitution of the Compounds of Chromium. II.** By GREGOIRE N. WYROUBOFF (*Bull. Soc. Chim.*, 1902, [iii], 27, 719—733. Compare this vol., ii, 565).—When an aqueous solution of sulphochromic acid is heated, a coagulum is formed which has the composition of *chromium sulphochromate*,  $[\text{Cr}_2\text{O}_2(\text{OH})_4(\text{SO}_2)_4\text{O}_2(\text{OH})_2]\text{Cr}_2(\text{OH})_6$ , and is identical with that obtained by precipitating a violet salt of chromium in the cold with sulphochromic acid. If this is maintained for some time in contact with boiling water, it becomes hydrated, dissolves slowly, and finally passes entirely into a solution of the green sulphate. Chromium sulphochromate, when heated at  $120^\circ$ , becomes soluble in water and the solution yields insoluble precipitates with metallic salts, *chromosulphochromates* being formed. These the author considers as ethers of the green sulphate in which two hydroxyl radicles have been replaced by sulphochromic acid. On adding hydrochloric acid to a solution of chromium sulphochromate, *chromosulphochromic acid*,  $[\text{Cr}_2\text{O}_2(\text{OH})_4(\text{SO}_2)_4\text{O}_3, \text{Cr}_2\text{O}(\text{OH})_2(\text{SO}_2)_3(\text{OH})_6](\text{OH})_2$ , is precipitated as a dark green, gelatinous mass which dissolves in water, yielding an opalescent solution. On adding 2 mols. of sulphuric acid and a little water to 1 mol. of chromium sulphochromate, evaporating on the water-bath, and heating for some hours at  $120^\circ$ , *chromodisulphochromic acid*,  $[\text{Cr}_2\text{O}_2(\text{OH})_4(\text{SO}_2)_4\text{O}_3]_2[\text{Cr}_2\text{O}(\text{OH})_2(\text{SO}_2)_3(\text{OH})_4](\text{OH})_4, \text{H}_2\text{O}$ , is obtained, which yields an insoluble salt with iron. With sulphochromic acid, chromium sulphochromate yields a chromosulphodichromate.

If chromium sulphate is heated with an excess of sulphuric acid to a temperature not exceeding  $150^\circ$ , a clear green, gelatinous precipitate of sulphochromic acid is formed; on continuing the heating and at the same time allowing the temperature to rise, the green precipitate gradually changes into a heavy, greyish-yellow powder, soluble in water, yielding a milky, strongly acid solution. The same substance is obtained by heating sulphochromic acid for some time at  $250^\circ$ , and is the first anhydride of a polymeride of chromosulphochromic acid.

The author also points out that although sulphochromic acid forms insoluble compounds with the metals, it does not give precipitates with all the salts of the metals. Thus, it gives a precipitate with a solution of mercuric nitrate or acetate, but not with mercuric bromide. The author explains this by saying that the last-named salt is an anhydride and not a normal salt.

The author also gives details as to the method employed in the analysis of the compounds described. A. F.

**Colour Reaction of Uranium Salts with Hydrogen Peroxide.** By JULES F. ALOY (*Bull. Soc. Chim.*, 1902, [iii], 27, 734—735).—On adding to the solution of any uranium compound a little hydrogen peroxide and then potassium carbonate, either solid or in very con-

centrated solution, a fine red coloration is developed; on adding alcohol, the red compound is precipitated. This reaction may also be made use of for the detection of hydrogen peroxide. The red compound is very unstable, but the author has obtained apparently crystalline compounds of uranium by treating the solution with methyl instead of ethyl alcohol. A. F.

**Vanadium Silicide.** By HENRI MOISSAN and HOLT (*Compt. rend.*, 1902, 135, 78—81).—Vanadium silicide,  $\text{VSi}_2$ , is obtained by heating an intimate mixture of vanadium trioxide with a little more than five times its weight of silicon for about 2 minutes in an electric furnace with a current of 50 volts and 1000 amperes, and treating the residue successively with potassium hydroxide solution and strong nitric or sulphuric acid. It can also be obtained by reducing a mixture of silicon and vanadium trioxide with magnesium. It forms brilliant prisms which have a metallic lustre and a sp. gr. of 4.42, scratch glass, and melt and volatilise in the electric furnace. Alkalis and acids, with the exception of hydrofluoric acid, have no action on it, but it burns in fluorine, chlorine, or bromine when heated. Iodine vapour, oxygen, sulphur, and hydrogen sulphide attack it very slowly at the melting point of glass, but hydrogen chloride converts it into silicochloroform and vanadium chloride. Fused alkali hydroxides decompose the silicide; the action of fused metals depends on whether they combine more readily with silicon or with vanadium. Copper, for example, yields copper silicide and a copper vanadium alloy. C. H. B.

**Liquid Hydrosol of Gold.** By ALEXANDER GUTBIER (*Zeit. anorg. Chem.*, 1902, 31, 448—450).—A pseudo-solution of gold is obtained by reducing a very dilute solution of auric chloride with hydrazine hydrate in the cold. When the reduction is properly carried out, the solution is blue and keeps well, but when an excess of hydrazine is added the gold quickly separates.

By this reduction process, pseudo-solutions of silver, copper, lead, selenium, and tellurium can also be prepared. J. McC.

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### Mineralogical Chemistry.

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Large Crystals of Carnallite from Beienrode. By HUGO BÜCKING (*Jahrb. Min.*, 1902, ii, Ref. 12; from *Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 539—542).—A description, with goniometric and optical measurements, is given of wine-yellow crystals of carnallite, which measure 8 cm. long and 6 cm. thick. Analysis, by Kleinfeldt, gave :

Mg.	K.	Cl.	H <sub>2</sub> O.	Total.
8.80	13.51	38.16	39.53	100.00

L. J. S.

**Arsensulfurite.** By FRIEDRICH RINNE (*Centr. Min.*, 1902, 499—500).—This new mineral substance occurs as a very thin, brownish-red incrustation on andesitic lava from the active volcano of Papandajan in Java. The surface is usually smooth and bright, but sometimes the material is vesicular. Thin splinters are reddish-yellow and optically isotropic. Analysis by Y. Buchholz shows it to contain: S, 70.78; As, 29.22 per cent. For naturally occurring amorphous sulphur the name *sulfurite* is proposed, and for the arsenical variety now described, *arsensulfurite*.  
L. J. S.

**Mineralogical Notes.** By ALBERT H. CHESTER (*Jahrb. Min.*, 1902, i, Ref. 360—361; from *Ann. Rep. State Geologist, New Jersey*, for 1900, 1901, 175—188).—Notes are given of various minerals from New Jersey, and analyses of the following. Fahlerz (I) as small masses, with calcite and dolomite, at Southtown. Jamesonite (II) as lamellar masses, on Jenny Jump Mountain.

	Sb.	Cu.	Fe.	Zn.	Bi.	Pb.	S.	Cl.	CaO.	MgO.	SO <sub>3</sub> .	Insol.	Total.
I.	15.90	45.20	5.70	1.10	0.22	—	23.28	0.29	1.04	0.30	3.43	3.84	100.30
II.	29.60	—	—	—	—	52.16	15.79	—	—	—	—	1.29	98.82

A cupriferous ochre (III) as a dark-brown, powdery substance, resembling wad, occurs with copper ores at Bound Brook. Vesuvianite (?) (IV) as white, granular masses, with garnet and axinite at Franklin Furnace; sp. gr. 2.78; lustre, pearly. Deweylite (V) as yellowish-brown crusts on serpentine at Hoboken.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CuO.	MnO.	CaO.	MgO.	K <sub>2</sub> O.
III.	58.00	20.50	8.30	2.52	3.30	1.80	0.14	1.36
IV.	39.08	16.43	3.19	—	3.68	29.88	0.30	—
V.	38.20	0.80	0.94	—	—	4.76	31.32	—

	Na <sub>2</sub> O.	H <sub>2</sub> O at 100°.	H <sub>2</sub> O ignition.	SO <sub>3</sub>	B <sub>2</sub> O <sub>3</sub> .	Cl.	CO <sub>2</sub> .	Total.
III.	0.58	1.86	1.54	—	—	—	—	99.90
IV.	—	0.22	6.61	0.07	0.28	—	—	99.74
V.	—	7.67	12.09	0.11	—	0.15	3.70	99.74

L. J. S.

**Koenenite.** By FRIEDRICH RINNE (*Centr. Min.*, 1902, 493—499).—This new mineral was found, intimately associated with halite, anhydrite and carnallite, in crevices in the clay of the salt deposits at Volpriehausen, in the Sollinger Wald, Hanover. It is red in colour, owing to enclosed scales of hæmatite, and has a perfect micaceous cleavage. Distinct crystals, which belong to the rhombohedral system, are rare, the mineral usually occurring as scaly crusts. It is optically uniaxial and positive; sp. gr. 1.98. After deducting halite (about 15 per cent.) and carnallite, the following analyses (I, by Sundmacher; II, by Y. Buchholz) give the formulæ Al<sub>2</sub>O<sub>3</sub>, 3MgO, 2MgCl<sub>2</sub>, 8H<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub>, 3MgO, 2MgCl<sub>2</sub>, 6H<sub>2</sub>O respectively.

	Al <sub>2</sub> O <sub>3</sub> .	MgO.	MgCl <sub>2</sub> .	H <sub>2</sub> O.
I.	17.79	21.10	35.70	25.41
II.	18.25	23.44	36.85	21.46

When heated in water for 80 hours, koenenite leaves a residue having the composition  $\text{Al}_2\text{O}_3, \text{MgO}, \text{H}_2\text{O}$ . By prolonged heating with ammonium chloride solution, it yields  $\text{Al}_2\text{O}_3, 2\text{H}_2\text{O}$ , and this on ignition gives anhydrous alumina. All these secondary products ("meta-koenenites") retain the scaly form of the original mineral, and are optically uniaxial but negative.

L. J. S.

**Uraninite from Joachimsthal.** By F. JANDA (*Chem. Centr.*, 1902, ii, 150; from *Oesterr. Zeit. Berg-Hütt.*, 50, 283—288).—General notes are given of the history and mode of occurrence of pitchblende at Joachimsthal, Bohemia, and of the technical applications of uranium for colouring glass, &c. The following analysis is given of a sample of ore; in some samples, the amount of  $\text{U}_3\text{O}_8$  reaches 79.2 per cent.

$\text{U}_3\text{O}_8$	$\text{As}_2\text{S}_3$	PbS.	PbO.	$\text{Cu}_2\text{S}$	$\text{Bi}_2\text{S}_3$	$\text{Ag}_2\text{S}$	$\text{Fe}_2\text{S}_3, \text{FeS}_2$	$\text{Fe}_2\text{O}_3$	$\text{FeCO}_3$
49.949	0.711	1.848	0.250	1.115	0.308	0.040	7.928	1.136	6.960

$\text{Al}_2\text{O}_3$	ZnO.	$\text{MnO}_2$	$\text{CaCO}_3$	$\text{CaSO}_4$	$\text{MgCO}_3$	$\text{MgSO}_4$	$\text{SiO}_2$	$\text{V}_2\text{O}_5$	$\text{H}_2\text{O}, \text{Na}_2\text{O}, \text{K}_2\text{O}, \text{P}_2\text{O}_5$
3.245	1.093	0.107	3.690	0.893	0.756	0.068	18.545	0.015	1.343

Also traces of lead sulphate, copper sulphate, nickel, molybdenum, tungsten, polonium, radium and actinium; cobalt, fluorine and rare earths are absent.

L. J. S.

**Melanterite from Falun, Sweden.** By J. EDV. EDGREN (*Jahrb. Min.*, 1902, ii, Ref. 29; from *Geol. För. Förh.*, 1901, 23, 329).—A description is given of crystals of melanterite from the workings of the Falun mine. Analysis, by L. G. Thomé, gave the following results, which correspond with the formula  $(\frac{6}{7}\text{FeO}, \frac{1}{7}\text{MgO})\text{SO}_3, 7\text{H}_2\text{O}$ :

FeO.	MgO.	$\text{SO}_3$	$\text{H}_2\text{O}$
22.27	1.87	29.19	45.79

L. J. S.

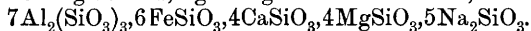
**A New Zeolite (Mooraboolite).** By G. B. PRITCHARD (*Victorian Naturalist*, 1901, 18, 63—65).—Cavities in the decomposed basalt, near Maude, in the Moorabool valley, Victoria, contain radial aggregates of a white to colourless mineral, which had previously been thought to be aragonite. The following characters, however, point to a zeolite allied to natrolite. Sp. gr. = 2.167—2.17; H = 6. The crystals show a long, rhombic prism terminated by a low pyramid; no cleavage is apparent. Analysis by E. O. Thiele gave:

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	CaO.	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{H}_2\text{O}$	Total.
48.024	28.684	0.42	11.239	3.001	9.8	101.68

L. J. S.

**Jadeitite from Cassine (Acqui).** By LUIGI COLOMBA (*Jahrb. Min.*, 1902, ii, Ref. 26; from *Riv. min. ital.*, 1901, 27, 18).—The material was found in the Bormida river. It shows, under the microscope, many pyroxene individuals which are partly altered to kaolin

and chlorite ; zircon, quartz and spinel (?) are rarely present. Analysis gave the following results, agreeing with the formula,



SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Loss on ignition.	Total.
55·98	18·02	trace	10·01	5·30	3·63	7·04	trace	0·27	100·27

L. J. S.

**Meteoric Iron from Surprise Springs, California.** By E. COHEN (*Mitth. naturwiss. Ver. Neu-Vorpommern u. Rügen*, 1902, 33, (1901), 29—33).—This iron, weighing 1524 grams, was found in 1899 at Surprise Springs, near Bagdad in San Bernardino Co. It is octahedral in structure. Sp. gr = 7·7308. Analysis gave :

Fe.	Ni.	Co.	Cu.	Cr.	S.	P.	C.	Cl.	Total.
91·01	7·65	0·89	0·07	0·04	0·08	0·22	0·02	0·02	100·00

L. J. S.



## Physiological Chemistry.

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'Survival' Respiration of Muscle. By W. M. FLETCHER (*J. Physiol.*, 1902, 28, 354—359).—The early stages of *rigor mortis* which are marked by a steady output of carbon dioxide are incomplete in the absence of oxygen. The rate of output is lessened by about 30 per cent. in an atmosphere of nitrogen (prepared from urea) as compared with air. The output is largely increased (from 80 to 300 per cent.) in an atmosphere of oxygen.  
W. D. H.

Elaboration of Zymogen in the Gastric Glands of the Viper *Berus*. By L. LAUNOY (*Compt. rend.*, 1902, 135, 195—197).—The elaboration of the zymogen grains is endonuclear; the formation of the grains in the gastric cells is independent of all reflex or mechanical action and takes place when the digestive tract has been left in a state of rest by starvation. The transformation of the zymogen into an enzyme is carried out in the cytoplasm and is due to some exciting external cause.  
J. McC.

The Mechanism of Pancreatic Secretion. By W. M. BAYLISS and ERNEST H. STARLING (*J. Physiol.*, 1902, 28, 325—353. Compare this vol., ii, 275).—A full account of the experiments previously published. The nature of secretin and prosecretin is not yet determined. Secretin causes some increase in the flow of bile, but does not act on any other glands except the pancreas and liver. Acid extracts of the intestinal mucous membrane contain also a substance which produces a fall (not a rise, as erroneously stated in the previous abstract) of blood pressure. Secretin may be prepared free from this depressor substance by acting on desquamated epithelial cells with acid.

W. D. H.

**Action of Peptone and Secretin on the Pancreas.** By A. HERZEN and C. RADWIKOWSKI (*Compt. rend. Soc. Biol.*, 1902, 54, 507—509).—Intravascular injection of peptone in dogs acts on the pancreas only as a succagogue, whilst that of secretin acts both as a succagogue (increasing the flow of juice) and as a trypsinogen (that is, converting the zymogen of trypsin into the active enzyme). The internal secretion of the spleen acts in the same way on the zymogen in the pancreas itself; secretin or enterokinase acts normally in the intestine on the zymogen secreted as such by the pancreas.

W. D. H.

**Influence of Various Reagents on the Activity of Pancreatic Diastase.** By PAUL GRUTZNER and M. WACHSMANN (*Pflüger's Archiv*, 1902, 91, 195—207).—Glycerol extracts of pigs' pancreas were employed, and their power to convert starch into sugar tested when various additions were made to the mixture. With increasing concentration, sodium chloride, bromide, and iodide first hasten and then lessen the action; sodium fluoride favours the action until a strength of 4 per cent. is reached, when it is no longer soluble. Alkalis and alkali salts act inhibitingly even in the weakest solutions. The sulphates of sodium, magnesium, and ammonium, and mercuric chloride are specific poisons for this ferment. Acids first increase and then lessen its action. The results are shown in the form of curves, and these are different for different acids. Chloroform, alcohol, ether, and thymol all act inhibitingly, especially the first-named. Among animals, the diastatic ferment of the pig is the most active, then follow the rat, rabbit, ox, sheep, and cat, in the order named.

W. D. H.

**Lymph Formation and Bile Secretion.** By ALEXANDER ELLINGER (*Beitr. chem. Physiol. Path.*, 1902, 2, 297—306).—From the experiments described, which consisted in observing the amount of bile poured out from a permanent fistula in dogs during the injection of lymphagogues (peptone, leech extract), the conclusion of Asher and Barbèra that there is a causal relationship between bile secretion and lymph formation is disputed.

W. D. H.

**Formation of Higher Fatty Acids from Sugar.** By A. MAGNUS-LEVY (*Chem. Centr.*, 1902, i, 1410; from *Arch. Anat. Physiol. ; physiol. Abth.*, 1902, 365—369).—Great importance is attached to the fact that in autolysis of the liver small quantities of acetic and hexoic acids are formed. The lower acids are capable of forming the higher, acetaldehyde being regarded as an intermediate product. The following equations represent this in the case of lactic acid,  $9\text{C}_3\text{H}_6\text{O}_3 = 9\text{C}_2\text{H}_4\text{O} + 9\text{H}_2 + \text{CO}_2$ ;  $9\text{C}_2\text{H}_4\text{O} + 7\text{H}_2 = \text{C}_{18}\text{H}_{36}\text{O}_2 + 7\text{H}_2\text{O}$ . This is believed to explain the formation of fat from carbohydrate in the body.

W. D. H.

**Enterokinase and Secretin.** By LUCIEN CAMUS (*Compt. rend. Soc. Biol.*, 1902, 54, 513—515).—Enterokinase and secretin are not identical; one may be present without the other in extracts of the

intestine, and acid which changes prosecretin into secretin has no such influence in producing enterokinase.

W. D. H.

**Kinases of Microbic Origin.** By C. DELEZENNE (*Compt. rend.*, 1902, 135, 252—255).—Certain bacterial growths are shown to be capable of producing an enzyme which acts on the pancreatic juice in the same way as does the enterokinase obtained by Pawloff from intestinal juice.

W. D. H.

**Influence of the Spleen on Pancreatic Digestion.** By LAFAYETTE B. MENDEL and LEO F. RETTGER (*Amer. J. Physiol.*, 1902, 7, 387—404).—These experiments were undertaken with the view of testing the truth of the Schiff-Herzen hypothesis. Extracts of spleen, prepared from the organ when congested during digestion, increase the proteolytic power of the pancreas, both *in vitro* and *in vivo*. Defibrinated blood from the splenic vein has the same effect. Extracts of liver and pancreas have but little action in this direction. The precipitate produced by adding alcohol to splenic extracts contains a trypsinogenic substance. Extracts of the pancreas of dogs without a spleen are not always free from trypsin. Extirpation of the spleen produces, in fact, no interference with digestive or other functions. The "activating" influence of intestinal juice is most important. The physiological importance of the spleen in the process is questionable.

W. D. H.

**The Proteolytic Enzyme of the Spleen.** By J. B. LEATHES (*J. Physiol.*, 1902, 28, 360—365).—The products of the action in an acid medium of the proteolytic enzyme found in the cell juice of the spleen of oxen are the same as those formed by trypsin in alkaline media, or those formed by the hydrolytic action of mineral acids. The physiological significance of such enzymes in metabolism is discussed. The fact that acid is favourable to its action fits in with Ehrlich's view that the reaction of the nucleus in living cells is acid. Intracellular proteid katabolism is probably a reversion of anabolism. The autolysis of proteid in muscles, spleen, &c., provides the heart and nervous system during starvation with identical substitutes for the digestive products of proteid food.

W. D. H.

**The Influence of Muscular Work on Metabolism.** By IGO KAUP (*Zeit. Biol.*, 1902, 43, 221—255).—Three experiments on men are fully described; the influence of work on nitrogenous metabolism is *nil*. The amount of phosphoric acid secreted is less during work than during rest.

W. D. H.

**Influence of abundant Proteid Food on Metabolism.** By OTTO FRANK and R. TROMMSDORFF (*Zeit. Biol.*, 1902, 43, 258—287).—The experiment was made on a dog. The influence of increased proteid nutriment on nitrogenous and carbonaceous metabolism is described in full. Attention is also paid to the production of heat.

W. D. H.

**Trypsin.** By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1902, 35, 545—549).—Polemical. The statement made by Kutscher that the formation of hexon bases is characteristic of tryptic action is disputed.  
W. D. H.

**A Ferment in Leucocytes and Lymph Glands which favours Tryptic Activity.** By C. DELEZENNE (*Compt. rend. Soc. Biol.*, 1902, 54, 283—285).—An extract of lymph glands or of leucocytes liquefies gelatin, but has no other action by itself on proteids. Added to pancreatic juice, it reinforces the action of trypsin in the same way as enterokinase.  
W. D. H.

**Behaviour of  $\alpha$ -Glucoheptose in the Animal Body.** By JULIUS WOHLGEMUTH (*Zeit. physiol. Chem.*, 1902, 35, 568—579).—Given to rabbits by the mouth, subcutaneously or intravenously, from 30—50 per cent. of  $\alpha$ -glucoheptose is excreted in the urine unchanged. After the animals had been starved and 6 grams of  $\alpha$ -glucoheptose given, the liver contained in these experiments 0.2, 0.36, and 0.48 gram of glycogen, and 0.42, 0.37, and 0.50 gram of sugar respectively.  
W. D. H.

**Fate of Uric Acid introduced into the Stomach.** By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1902, 35, 495—513).—If uric acid is introduced into the stomach of dogs, a variable fraction (20—47 per cent.) is absorbed. Of this, a large part is excreted as allantoin, the rest as urea. In rabbits, it is mostly absorbed; a small part is excreted unchanged, a small part as allantoin, and the rest as urea. This conflicts with the results of Soetbeer and Ibrahim (this vol., ii, 337).  
W. D. H.

**Glycuronic Acid Excretion.** By PAUL MAYER (*Chem. Centr.*, 1902, i, 1408; from *Arch. Anat. Physiol.*; *Physiol. Abth.*, 1902, 342—347).—In rabbits in which artificial dyspnoea has been produced, large quantities of glycuronic acid are excreted, but there is no corresponding increase in the secretion of indole and phenol. The administration of large quantities of sugar produces the same result. The experiments of other workers on the subject are criticised.  
W. D. H.

**The Fate of Sodium Thiocyanate in the Organism.** By LEO POLLAK (*Beitr. chem. Physiol. Path.*, 1902, 2, 430—433).—In view of Raudnitz's statement that outside the body superoxydases decompose thiocyanates with the formation of hydrocyanic acid, experiments were made by giving both to animals and man, either by the mouth or subcutaneously, weighed amounts of sodium thiocyanate. In the course of a few days, it was practically all recovered from the urine unchanged. In the dog, none was found in the salivary glands or pancreas. The 'surviving' liver, like the living body, has also no power of decomposing thiocyanates.  
W. D. H.

**Excretion of Sodium Chloride after Extirpation of the Pancreas.** By RAPHAEL LÉPINE and MALTET (*Compt. rend. Soc. Biol.*, 1902, 54, 404—405).—In ordinary glycosuria, there is no increase of

sodium chloride in the urine, but an increase does occur in the glycosuria which follows extirpation of the pancreas. W. D. H.

**Influence of Phloridzin on the Elimination of Sodium Chloride.** By RAPHAEL LÉPINE and MALTET (*Compt. rend. Soc. Biol.*, 1902, 54, 404).—Small doses of phloridzin in dogs, insufficient to cause glycosuria, do not increase the amount of sodium chloride in the urine. Larger doses render the kidney more permeable, not only to sugar, but also to sodium chloride. W. D. H.

**The Relation of Adenine and Guanine in the Organism.** By ALFRED SCHITTENHELM (*Chem. Centr.*, 1902, i, 1306; from *Arch. exp. Path. Pharm.*, 47, 432—437).—Minkowski showed that, in dogs, feeding with adenine, in contradistinction to hypoxanthine, produces no increase of uric acid or allantoin excretion. Nevertheless, it produces poisonous symptoms, and the formation of calculi of uric acid and ammonium urate in the kidneys. The present research on rabbits shows that feeding with adenine produces no rise in uric acid excretion; 24.2 per cent. of the adenine given is excreted unchanged. Relatively large doses produce the same symptoms as in dogs. Guanine given to rabbits produces neither increase in purine excretion nor pathological changes in the kidneys. W. D. H.

**Effect of Compression of the Ureter on the Urine.** By M PFAUNDLER (*Beitr. chem. Physiol. Path.*, 1902, 2, 336—343).—In dogs, the urine was collected from the ureter, which was then compressed, and the urine again examined. A few cases in man, in which such an observation was possible, are also given.

Under the influence of the compression the pressure rises, and the amount of urine increases, but its molecular concentration falls greatly, to a half or three-quarters that of the original. Four per cent. of this decrease is due to urea, 11 to sodium chloride, and the remaining 85 per cent. to substances not estimated, but probably of inorganic nature because of the great lessening of electrical conductivity. W. D. H.

**Glycogen of the Heart.** By PAUL JENSEN (*Zeit. physiol. Chem.*, 1902, 35, 514—524; 525—535).—The normal percentage of glycogen in the heart varies between 0.3 and 0.5. In starved dogs in which the amount of glycogen had sunk in the leg muscle to 1/10—1/30 of the normal, that in the heart had not as a rule diminished. The diaphragm behaves usually like the limb muscles in this respect. In one case, no glycogen was found in the heart, but, nevertheless, this organ continued to beat. In the liver, the percentage of glycogen in one case (17 days' inanition) was 2.4; in another (19 days) 0.08. The reserve glycogen of the heart is of obvious physiological significance. From observations in frogs, it is held that after the entire disappearance of glycogen from the heart (produced by doses of strychnine), the glycogen returns nearly to the normal even if no food is given. A colorimetric method with iodine for estimating small quantities of glycogen is described.

W. D. H.

**Glycogen during Inanition.** By EDUARD PFLÜGER (*Pflüger's Archiv*, 1902, 91, 119—134).—A dog was kept without food for 28 days. It had lost 24 per cent. of its weight, and was then killed. The glycogen reckoned as sugar was then estimated, with the following results:

Organ.	Weight of organ.	Grams of sugar obtained.
Liver.....	507 grams.	24·26
Muscles.....	13,130 „	20·75
Bones .....	— „	5·89
Skin .....	5100 „	1·40
Blood.....	2083 „	0·19
Other parts .....	2693 „	traces

If the loss of glycogen due to the necessary delay before the analysis was commenced, and the sugar from gluco-proteids are allowed for, probably 100 grams of sugar in all would have been obtainable from an animal in an advanced state of inanition.

W. D. H.

**Analysis of Nervous Tissue.** By N. ALBERTO BARBIERI (*Compt. rend.*, 1902, 135, 246—248).—The substances are divided into three groups, which are stated to be quite distinct; (1) substances soluble in ether; (2) substances soluble in ether-water; and (3) the residue. The percentage of phosphorus in each is given as different, and is apparently considered to be a fixed value.

W. D. H.

**Iron in the Blood of the Newly-born.** By MAURICE NICLOUX and VAN VYVE (*Compt. rend. Soc. Biol.*, 1902, 54, 581—583).—The analytical results given in tabular form show that the amount of iron in the blood of those born at full term averages 0·45 gram per 1000 gram of blood; for those born before full term, the proportion is very similar (0·47:1000). In cases where albuminuria exists, the proportion falls to 0·38:1000, and in fœtuses born dead, it falls to half the normal.

W. D. H.

**Calcium and Magnesium in the Dog.** By JULES ALOY (*Compt. rend. Soc. Biol.*, 1902, 54, 604—605).—The analyses presented show that magnesium preponderates in the cells and 'noble' tissues, and that calcium preponderates in the connective or skeletal tissues. The importance of the former metal in living processes is believed to be greater than that of calcium.

W. D. H.

**Combination of Copper in the Liver.** By B. SLOWITZOFF (*Beitr. chem. Physiol. Path.*, 1902, 2, 307—311).—Previous researches have shown that, in the liver, arsenic unites with the nuclein, and mercury with the globulin. Copper also unites with the nuclein. The copper nucleinate is not affected by 2 per cent. solution of sodium hydroxide, but is decomposed by 0·3 per cent. hydrochloric acid, or by pepsin-hydrochloric acid.

W. D. H.

**Iron in Hen's Eggs.** By C. HARTUNG (*Zeit. Biol.*, 1902, 43, 195—212).—By giving iron oxide mixed with the food to hens, the

amount of iron in the eggs laid increases considerably after some months. Full analytical details are given. The disadvantage of these 'iron eggs' for therapeutic purposes is their expense. W. D. H.

**Ammonia and Lactic Acid in the Blood of Geese.** By KATH. KOWALEWSKY and SERGEI SALASKIN (*Zeit. physiol. Chem.*, 1902, 35, 552—567).—The amount of ammonia in the blood of geese is higher than in that of the dog, and is fairly constant. Administration of even large quantities of alkalis does not alter it much. It increases if poisonous doses of acid are given. On administration of alkalis, the alkalinity of the blood (Salkowski-Salaskin method) does not alter, excess being rapidly eliminated in the urine; it lessens if acids are given. In pathological cases, when the alkalinity of the blood is less than normal, administration of alkali raises the alkalinity, excess being retained in the blood, and it is not rapidly excreted. The estimations of lactic acid were not very numerous, but the results show that its amount is but little altered by giving either acid or alkali. Large doses of acid probably raise its amount; this is deduced from observations on gaseous metabolism.

The effects on the urine are as follows: alkalis increase the uric acid nitrogen, lessen the ammonia nitrogen, and leave the urea nitrogen practically unchanged. Acids diminish the uric acid nitrogen, increase the ammonia nitrogen, and slightly increase the urea nitrogen. In normal circumstances, urea is in great part converted into uric acid by birds. This change is not increased by alkalis, but is lessened by acids.

After giving alkalis, lactic acid appears in the urine. This is related to the interference produced on gaseous interchanges.

W. D. H.

**Glycuronic Acid in Dog's Blood.** By RAPHAEL LÉPINE and BOULUD (*Compt. rend.*, 1902, 135, 139—140).—Further experiments are adduced to show that the blood (and liver) of the dog contains conjugated glycuronic acid. The amount increases when the blood is defibrinated. Boiling in the presence of acid usually lessens the amount, owing to the easy way in which these compounds are broken up.

W. D. H.

**Variation in the Iodine of the Blood.** By EUGÈNE GLEY and PAUL BOURCET (*Compt. rend.*, 1902, 135, 185—186).—Iodine is stated to be a normal constituent of the blood. It is supposed to be of alimentary value and to originate in the thyroid. The amount is very variable. It is lessened and finally disappears after excessive bleeding, but on feeding reappears in 20 days. The observations recorded were made on dogs.

W. D. H.

**The Influence of Altitude on the Blood.** By EMIL ABDERHALDEN (*Zeit. Biol.*, 1902, 43, 125—194).—The observations were made on animals transferred from Basle to St. Moritz. The influence of the greater altitude in producing an increase in red corpuscles, in total hæmoglobin, and in hæmoglobin per corpuscle is supported by a large

amount of analytical evidence. The change occurs rapidly, and the reverse change takes place equally rapidly on a return to Basle. Histological alterations in the red corpuscles, and any difference in the iron reaction of the tissues, were not noted. W. D. H.

**The Decomposition of Potassium Iodide in the Organism by Nitrites.** By A. STEPANOFF (*Chem. Centr.*, 1902, i, 1306; from *Arch. exp. Path. Pharm.*, 47, 411—416).—Various organs of the rabbit, when kept on milk, a food free from nitrates, show no nitrite reaction; but if nitrates are given also, they do. The reduction of nitrates to nitrites in the body is believed to be of a fermentative nature. The presence of nitrites is believed to be essential to the therapeutic value of potassium iodide. W. D. H.

**Indoxyluria.** By FERDINAND BLUMENTHAL (*Chem. Centr.*, 1902, i, 1408; from *Arch. Anat. Physiol.*; *Physiol. Abth.*, 1902, 347—351).—Experiments on rabbits in inanition, and on various diets, show that with increased proteid katabolism, indoxyl appears in the urine, and the conclusion is drawn that the intervention of bacteria is not necessary for the production of indoxyl. W. D. H.

**Influence of the Methyl Group on the Toxicity of various Organic Metallic Compounds.** By MARC LAFFONT (*Compt. rend. Soc. Biol.*, 1902, 54, 286—288).—Experiments were made on guinea-pigs regarding the toxicity of sodium dimethylarsinate and disodium monomethylarsinate, and the conclusion is drawn that the methyl group plays the part of a haptophore, to use Ehrlich's nomenclature; the presence of a second methyl group increases the production of free receptors, and the leucocytes will fix the metallic compound more readily, and so the toxicity of the compound is decreased. W. D. H.

**Physiological Action of Organic Ammonium Iodides and Polyiodides.** By C. JACOB (*Chem. Centr.*, 1902, i, 1306; from *Nachr. k. Ges. Wiss. Göttingen*, 1902, 108—113).—Rosenbach stated that tetramethylammonium tri-iodide gives clinically favourable results in the treatment of wounds, when used in small quantities instead of iodoform. The present research shows that, in animals, this substance in large doses produces toxic symptoms resembling those caused by curare and muscarine. Tetramethylammonium iodide, and valeryl- and isoamyl-trimethylammonium chloride produce the same symptoms. Tetraethylammonium tri-iodide has the same local action as the methyl compound, but produces none of the poisonous effects. W. D. H.

**Physiological Action of Borax and Boric Acid; its Use as a Preservative of Foods.** By E. ROST (*Chem. Centr.*, 1902, ii, 139—140; from *Arb. Kais. Ges. A.*, 19, 1—70). By MAX RUBNER (*ibid.*, 140—141; from *ibid.*, 70—88). By R. O NEUMANN (*ibid.*, 141; from *ibid.*, 89—96). By ARTHUR HEFFTER (*ibid.*, 141; from *ibid.*, 97—109). By EDUARD POLENSKE (*ibid.*, 141—142; from *ibid.*, 167—168).—The



general effect of these extensive experiments is to show the harmful effects of borax and boric acid, even in such quantities as are used in preserving foods.  
W. D. H.

**Antitoxic Effect of Ions.** By HUGH NEILSON (*Amer. J. Physiol.*, 1902, 7, 405—408).—Small amounts of salts with uni-, bi-, or tri-valent kations diminish the poisonous effect of the chlorides of sodium, lithium, ammonium, and potassium on voluntary muscle; figures are given where the best results are obtained. Sodium salts with anions of higher valency when added to solutions of sodium or lithium chloride have no antitoxic effect, but have a slight antitoxic effect when added to solutions of ammonium or potassium chloride.

W. D. H.

**The Effect of Calcium and of Free Oxygen on Rhythmic Contraction.** By S. S. MAXWELL and J. C. HILL (*Amer. J. Physiol.*, 1902, 7, 409—411).—The ciliated cells of the frog's œsophagus remain active in 1/8 *N*-calcium chloride solution for many hours. The average duration of activity in boiled solutions was 31 hours; in solutions saturated with oxygen, 20 hours. The oxygen factor has been hitherto neglected in such experiments, and may explain some discrepancies.

W. D. H.

**Oxidative Properties of the Cell-nucleus.** By RALPH S. LILLIE (*Amer. J. Physiol.*, 1902, 7, 412—421).—A general similarity exists between the distribution of nuclear matter in the various tissues of the frog, and the distribution of coloured synthetical products formed within the same tissues by their oxidative action. In a number of instances, especially liver, kidney, and blood corpuscles, the coloured products are deposited chiefly in and about the nucleus, especially at the surface of contact between the nucleus and the cytoplasm.

W. D. H.

**Artificial Parthenogenesis in Annelids.** By MARTIN H. FISCHER (*Amer. J. Physiol.*, 1902, 7, 301—314).—Experiments on *Amphitrite* and *Nereis* confirm Loeb's hypothesis that the spermatozoon does not act as a stimulus to the egg that starts its development, but as a catalyser which accelerates a process that starts of its own accord.

W. D. H.

**Antiurease.** By LEOPOLD MOLL (*Beitr. chem. Physiol. Path.*, 1902, 2, 344—354).—This is a research in which the question was investigated whether the enzyme of the *Micrococcus ureae* is capable of stimulating the production of an anti-substance as so many other enzymes do. Normal serum has some inhibiting influence on the ferment, but this varies, and is not due to inorganic salts. Immunisation was produced by gradually increasing injections in animals, and the serum became strongly inhibitory in its action. The antiurease to which this is due is destroyed by heating for an hour at 65°, but not at 56°.

W. D. H.

A Fibrinogenous Substance in Egg-white. By ARMAND GAUTIER (*Compt. rend.*, 1902, 135, 133—139).—It is well known that, on agitation, white of egg deposits a precipitate which has many of the solubilities of fibrin, and is membranous. The present communication advances the theory that the formation of this fibrin-like material is analogous to that of fibrin-formation in blood in being due to ferment activity. Agitation is stated not to be necessary. W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**The Zymase of *Eurotiosis Gayoni*.** By PIERRE MAZÉ (*Compt. rend.*, 1902, 135, 113—116).—The zymase of *Eurotiosis Gayoni* develops only in presence of air. The proportion of zymase for a given quantity of mycelium varies considerably, but is highest in young cultivations and disappears as the growth of the organism proceeds. C. H. B.

**The Nitrogenous Constituents of Certain Fungi.** By ERNST WINTERSTEIN and J. HOFMANN (*Beitr. chem. Physiol. Path.*, 1902, 2, 404—410).—The main fungus investigated was *Boletus edulis*, but *Agaricus campestris*, and *Cantharellus cibarius* were also examined. The residue, obtained from an extract made with light petroleum, consists largely of proteid. By decomposition with acids, hexon bases were obtained. W. D. H.

**Effect of Kainite as Manure on the Germination and Growth of Various Plants.** By KARL ENNENBACH (*Bied. Centr.*, 1902, 31, 559—565; *Inaug. Diss. Bâle*, 1901).—The results of experiments with various plants showed that kainite supplies potassium in a readily available form and that any injurious action it may have is not due to impurities, but probably to its action on the physical properties of the soil. N. H. J. M.

**Relation of Calcium and Magnesium to Plant Growth.** By OSCAR LOEW and D. W. MAY (*Bied. Centr.*, 1902, 31, 552—553; from *Bul. Bur. Plant Ind. U.S. Dept. Agric.*, 1901, No. 1).—Calcium is required by plants in producing nucleo-albumin compounds and is deposited in the plant. Magnesium acts as a carrier of phosphoric acid and is migratory, the same quantity exercising its functions over and over again. Excessive assimilation of calcium hinders the assimilation of phosphoric acid owing to the production of calcium phosphate in the place of magnesium phosphate. In the case of some plants, the excess of calcium is rendered harmless by being precipitated as oxalate or carbonate.

When magnesium is present in excess, it may take the place of calcium in the nucleo-albumin compounds. Only very few plants have

the power of rendering magnesium compounds insoluble, but its injurious effects can be prevented by supplying an excess of calcium.

The results of analyses of soils from all parts of the world showed that whilst the relations of calcium and magnesium vary greatly, most soils, and all fertile ones, contain more calcium than magnesium.

Of the different plants in which magnesium has been determined, sugar beet (roots, leaves, and seeds) contains the highest percentage.

N. H. J. M.

**Relation of Calcium and Magnesium to Plant Growth.** By D. W. MAY (*Bied. Centr.*, 1902, 31, 554—555; from *Bul. Bur. Plant Ind. U.S. Dept. Agric.*, 1901, No. 1).—In water-culture experiments with various plants, the presence of 0.1 per cent. of soluble magnesium compounds killed the plants. The same amount of magnesium was without effect in presence of 0.2 per cent. of calcium.

Plants grown in sand were greatly injured by 1 per cent. of magnesium. The poisonous action was prevented by adding gypsum, but not by calcium carbonate.

In experiments with sandy loam, it was found that oats and beans grew best in presence of 0.8 per cent. of lime and 0.2 per cent. of magnesia (both as carbonate); less than 0.6 per cent. of lime, with more than 0.4 per cent. of magnesia, caused the destruction of the plants. When, however, the calcium was applied as sulphate, the plants grew well.

N. H. J. M.

**Action of Inorganic Salts on the Development and Form of Plants.** By GEORGE H. PETHYBRIDGE (*Bied. Centr.*, 1902, 31, 556—558; from *Inaug. Diss. Göttingen*, 1899).—Sodium chloride, when added to normal nutritive solutions in which wheat was grown, produced the same effect as dilution, reducing the diameter of the roots and stems and increasing the thickness of the cells of the endoderm and of the central cylinders of the roots, stems, and leaves, as well as the absolute number of fibres in the leaves. Similar results were obtained with maize and oats.

Calcium salts promote root development. Whilst potassium nitrate was favourable, and calcium chloride injurious, to growth, the two salts together were very beneficial.

In pot experiments in which oats and wheat were grown in garden soil, it was found that absence of moisture resulted in a considerable reduction in the amount of roots and in the height of the plants.

N. H. J. M.

**Action of Potassium on Plant-life.** By H. WILFARTH, G. WIMMER, H. RÖMER, E. MAYER, F. KATZ, and G. GEISTHOFF (*Chem. Centr.*, 1902, i, 1304; from *Arbeit. d. Deut. Landw. Ges.*, 68, 1—106).—The experiments relate to the influence of potash and potassium salts on the life and growth of several plants (potatoes, tobacco, mustard, oats, &c.).

W. D. H.

**Respiration of Resting Plants.** By R. KOLKOWITZ (*Bied. Centr.*, 1902, 31, 573—574; from *Ber. deut. bot. Ges.*, 1901, 19, 285).—The

intensity of the respiration of dried barley grains was determined by measuring the expired carbon dioxide. Respiration, which was very slight when the amount of water was 10—11 per cent., increased considerably with 20 per cent. of water, whilst with 33 per cent. of water there was an evolution of 2000-c.c. of carbon dioxide per kilogram in 24 hours, an amount which could be much increased by raising the temperature and the percentage of oxygen in the air.

Crushed grain showed increased respiration, whilst grain which had been ground to coarse meal respired even after being heated for several hours at 100° and again moistened. The power of respiration was destroyed by thymol water and by mercuric chloride, but not by 96 per cent. alcohol or by toluene.

N. H. J. M.

**Decomposition of Carbon Dioxide by Insolated Leaves.** By PIERRE P. DEHERAIN and EM. DEMOUSSY (*Compt. rend.*, 1902, 135, 274—275).—The decomposition of carbon dioxide by detached leaves is readily demonstrated in the following manner. A bell jar (150—200 c.c.) containing the leaves is inverted over a saturated solution of carbon dioxide in such a manner as to remove all the air except about 50 c.c.; it is then completely immersed in a jar filled with a solution of carbon dioxide. The initial height of the liquid in the bell jar being marked, the increase in the volume of the gas is readily seen. The production of oxygen is finally shown by means of a glowing straw.

The results of several experiments showed that the volume of oxygen exactly equalled that of the carbon dioxide consumed, no hydrogen, carbon monoxide, or other compounds being produced.

N. H. J. M.

**Chlorophyllous Assimilation in Leaves when the Upper or Under Sides are Exposed to Light.** By ED. GRIFFON (*Compt. rend.*, 1902, 135, 303—305).—Assimilation varied considerably according to the side of the leaves exposed to light, being greater when the upper surface is exposed. The differences were, however, not so great as those observed by Boussingault. The differences are greatest in the case of thick leaves, and when the surfaces are exposed to direct sunlight. Under natural conditions, when the one surface is exposed to direct and the other to diffused light, the differences are only slight.

The results, indicating that the parenchyma is adapted to the function of assimilation, are probably explained by the hypotheses of Stahl and Haberlandt.

N. H. J. M.

**A Permanent Action which tends to produce a Negative Tension in the Vessels of Wood.** By H. DEVAUX (*Compt. rend.*, 1902, 134, 1366—1369).—The lower pressure in wood cells as compared with that of the air is partly due to the volume of the carbon dioxide produced being less than that of the oxygen consumed. This respiratory action is relatively slight, but it is unceasing.

N. H. J. M.

**Migration in Woody Plants.** By GUSTAVE ANDRÉ (*Compt. rend.*, 1902, 134, 1514—1517).—The results of analyses of horse chesnut

stems and leaves at four different periods, from 29th July to 16th November, showed that in the stems the total ash increased at first and then remained nearly constant, whilst in the leaves there was a progressive increase. Both potassium and phosphoric acid increased in the stems, and it is suggested that this migration from the leaves may extend to the older branches. Calcium increased both in stems and in leaves.

The total nitrogen increased during the whole period in the stems. In the leaves, there was an increase of nitrogen followed by a decrease. The saccharifiable carbohydrates increased in the stems from the first to the second period, after which they decreased, whilst the cellulose continued to increase until the end of the experiment. In the case of the leaves, both the saccharifiable carbohydrates and the cellulose decreased during the first period and increased again during the second.

N. H. J. M.

**Presence of Lecithin in Vegetables.** By CHARLES F. SCHLAGDENHAUFFEN and E. REEB (*Compt. rend.*, 1902, 135, 205—208).—The quantity of lecithin in vegetables has been variously given by different authors. The cause of this is to be found in the method of extraction. In the light petroleum, ether, or ether-alcoholic extract, the authors have identified calcium and manganese phosphates, and they attribute this to the formation of a soluble metallic glycerophosphate from the ordinary phosphate present in the soil.

J. McC.

**Presence of Rennet in Plants.** By MAURICE JAVILLIER (*Compt. rend.*, 1902, 134, 1373—1374).—The sap of *Lolium* yielded a substance having all the properties of rennet. The substance occurs in large numbers of plants, and was obtained from the following varieties: *Anthriscus vulg.*, *Plantago lanceolata*, *Capsella Bursa pastoris*, *Geranium molle*, *Ranunculus bulbosus*, *Medicago lupulina*, *Lamium hybridum*, *L. amplexicaule*, and *Philadelphus coronarius*.

N. H. J. M.

**The Amount of Nicotine, Wax, Resin, and Non-volatile Organic Acids in Tobacco Leaves at different Periods in the Growth of the Latter.** By RICHARD KISSLING (*Chem. Zeit.*, 1902, 26, 672—673).—The following percentages were obtained in the dry tobaccos:

	1.	2.	3.	4.	5.	6.	7.
Wax .....	0·414	0·331	0·444	0·378	0·270	0·248	0·297
Nicotine .....	0·15	0·21	0·36	0·45	—	0·54	0·60
Resin soluble in light petroleum.	1·90	1·89	1·99	1·92	2·78	2·40	2·01
"    "    ether .....	0·71	1·00	0·71	0·51	0·91	0·68	0·75
"    "    alcohol .....	2·35	2·85	2·54	1·13	4·26	2·67	3·21
Citric acid (anhydrous) .....	3·41	5·80	5·75	5·79	—	5·90	4·73
Malic acid     "    .....	4·98	6·34	6·08	6·21	—	5·17	5·36
Oxalic acid     "    .....	1·51	1·89	1·93	1·95	—	1·98	2·13

The first sample represented the tobacco at the time the young plants were bedded out; 2, after the leaves had formed; 3, shortly

before full-growth; 4, just after full-growth; 5, ready for gathering; 6, after gathering, and already dried; and 7, the fermented tobacco.

W. P. S.

**Necessity of Lime for Seedlings, especially at Higher Temperatures.** By LEOPOLD VON PORTHEIM (*Bied. Centr.*, 1902, 31, 574—575; from *Bot. Centr.*, 1901, 88, 282).—In opposition to Dehérain's statement that germinating beans develop completely in absence of calcium at a temperature of 30—35°, it was found in every case impossible to obtain complete development under these conditions; the seedlings as a rule drying at an earlier stage than when germination took place at the ordinary temperature in absence of calcium.

The injurious effects observed when calcium is absent were shown by Schimper to be due to the presence of potassium hydrogen oxalate. When the injured portions are brushed over with a solution of calcium nitrate, new roots are produced.

N. H. J. M.

**Soil Phosphates soluble in Water.** By TH. SCHLOESING, jun. (*Compt. rend.*, 1902, 134, 1383—1385).—Four different soils which were kept damp for four months were found to contain more phosphoric acid soluble in water than samples of the same soils which had remained in a dry condition.

In the case of manured soils, the soluble phosphoric acid will be chiefly derived from the phosphates supplied in the manure. Aqueous extracts of two samples of Rothamsted wheat soil,\* the one unmanured and the other supplied with mineral manure, yielded 7 and 109 milligrams of phosphoric acid respectively per kilogram of soil. The same samples contained 0.09 and 0.19 per cent. of phosphoric acid soluble in boiling hydrochloric acid.

N. H. J. M.

**Composition of Cow's Milk.** By L. MOERMAN (*Chem. Centr.*, 1902, ii, 138; from *Bull. Assoc. Belge chimistes*, 16, 147—151).—The object of the experiments was to ascertain the effect of work on the composition of cow's milk. Work lessens the amount of milk secreted, and raises the proportion of its solid constituents, but the results are not very definite.

W. D. H.

**Variation in [the Amount of] Phosphoric Acid according to the Period of Lactation.** By FRED. BORDAS and SIG. DE RACZKOWSKI (*Compt. rend.*, 1902, 135, 302—303).—The greatest amounts of phosphoric acid, lecithin, and glycerophosphoric acid are found in milk produced in the first month after calving, after which the quantities (percentage as well as actual) gradually decrease.

N. H. J. M.

\* The samples referred to were taken from Plot 3 and Plot 5 of Broadbalk Field in 1893 (October), and represent the first 9 inches of soil.

## Analytical Chemistry.

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**Gas Analysis by Combustion.** By WALTHER HEMPEL (*Zeit. anorg. Chem.*, 1902, 31, 445—447).—Combustion of methane with oxygen by explosion gives satisfactory results only when the mixture explodes neither too violently nor too feebly; it is, however, complete provided that a correct amount of oxygen has been added. It has been found that a mixture of methane and air may be passed several times through a red hot platinum capillary tube or over a red hot platinum spiral without complete combustion taking place; results obtained by this method can only be satisfactory if a large excess of oxygen is present or if hydrogen is added in order to make the mixture explosive (compare Gautier, *Abstr.*, 1900, ii, 469, 537).

J. McC.

[Determination of Iodine in Solutions containing Iodine and Hydriodic Acid.] By C. H. L. SCHMIDT (*Zeit. physiol. Chem.*, 1902, 35, 386—395).—A modified method for estimating hydriodic acid and iodine in the filtrates from iodinated proteids is described; it consists in estimating the free iodine by the aid of thiosulphate and the total iodine ( $I_2 + HI$ ) by the aid of standard silver nitrate.

It has been found that sodium thiosulphate reacts with iodic acid according to the equation  $10HIO_3 + 11Na_2S_2O_3 = 2NaI + 8NaIO_3 + Na_2S_2O_6 + 4Na_2S_4O_6 + Na_2SO_4 + 3S + 5H_2O$ , and a solution of the acid may therefore readily be standardised by the aid of *N*/20 thiosulphate (1 c.c. = 0.0079 gram iodic acid).

J. J. S.

**Estimation of Total Phosphoric Acid in Basic Slags.** By CAMILLE ASCHMAN (*Chem. Zeit.*, 1902, 26, 823).—A slight but essential modification of the method formerly proposed (*Abstr.*, 1899, ii, 807). The solution resulting from the treatment of the powdered slag with dilute nitric and sulphuric acid is filtered immediately instead of after 12 hours. Fifty c.c. of the filtrate are then at once mixed with 10 c.c. of the citric acid solution so as to prevent precipitation of calcium compounds. On adding ammonia previous to the magnesia mixture, the liquid should remain perfectly clear; should a flocculent precipitate of silicic acid form, the estimation should be repeated by another method, but this very rarely occurs. It sometimes happens that the liquid turns black after neutralisation or during the action of the magnesia mixture, but this colour gradually disappears on stirring. After stirring for 40 minutes, an hour or two should elapse before the precipitate is collected.

L. DE K.

**Analysis of Superphosphates.** By J. LEGRAND (*Chem. Centr.*, 1902, ii, 156; from *Bull. Assoc. Belge chimistes*, 16, 143—144).—In the analysis of superphosphates, it is frequently noticed that the filtrate after some time becomes turbid and opalescent. This precipitate, which disappears on adding a little nitric acid, is neither calcium



sulphate nor dicalcium phosphate, but consists chiefly of ferric phosphate with not more than 6—7 per cent. of aluminium phosphate, and a small quantity of ferrous phosphate. The precipitate is slowly soluble in ammonium citrate solution. L. DE K.

**Volumetric Estimation of the Double Phosphates of Ammonium with Cadmium, Cobalt, Manganese, and Zinc.** By HENRY D. DAKIN (*Zeit. anal. Chem.*, 1902, 41, 279—289).—Stolba's method for the volumetric estimation of magnesium ammonium phosphate (*Chem. Centr.*, 1866, 727) can be used with advantage for titrating the above double phosphates.

The precipitate is dissolved in an excess of *N*/10 sulphuric acid and the total acid titrated with *N*/10 sodium hydroxide, using methyl-orange as indicator. The change of colour occurs when the phosphoric acid is converted into a dihydric phosphate. The mode of precipitation should be that laid down by the author and by Miller and Page (*Abstr.*, 1900, ii, 624; 1901, ii, 131; this vol., ii, 49), but cadmium must be precipitated in the cold, since the precipitate will be deficient in ammonia if thrown down from a hot solution. The titration should take place at a temperature not exceeding 25°, and in the case of cobalt the solution to be titrated should not contain more than 0.1 gram of the double salt in 100 c.c. M. J. S.

**Colorimetric Estimation of Arsenious Acid.** By J. MAI (*Zeit. anal. Chem.*, 1902, 41, 362—365).—Arsenious acid is heated with fuming hydrochloric acid in a slow current of dry carbon dioxide, and the arsenious chloride which distils over converted into sulphide by impinging on the surface of a piece of calico wetted with a strong aqueous solution of hydrogen sulphide. The calico is tied over the mouth of a funnel-shaped vessel, which is inverted in the basin containing the hydrogen sulphide solution, and just touches the surface of the liquid. It is necessary to pierce a few holes in the calico with a needle to allow the carbon dioxide to escape freely, otherwise the pressure of the gas forces the precipitate through the fabric. It is important to avoid distilling over aqueous hydrochloric acid with the arsenious chloride. With amounts of from 0.1 to 0.6 mgm. of arsenious oxide, differences of 0.1 mgm. are easily distinguished. M. J. S.

**The Marsh-Berzelius Arsenic Deposit.** By WILLIAM ACKROYD (*J. Soc. Chem. Ind.*, 1902, 21, 900—901).—To obtain uniformly brown deposits of arsenic, the current of hydrogen should be slow, combined with a sparing evolution of arsenic hydride, the latter condition being brought about by the gradual addition of the arsenical substance to the Marsh apparatus. The rate of the hydrogen current may be judged by the size of the flame at the open end of the tube. Blue deposits of arsenic were usually observed when inorganic substances were tested, and the author concludes that in this state the particles are larger than in the brown deposits. W. P. S.

**Methods for Arsenic Estimation in Malt Liquors, &c.** By FREDERIC W. RICHARDSON (*J. Soc. Chem. Ind.*, 1902, 21, 901—903).—The

author prefers a modification of the Gutzeit test to the Marsh-Berzelius method, and chars the malt liquor with a mixture of sulphuric and nitric acids, removing the latter by evaporation and the addition of ferrous sulphate when fuming commences, before applying either test. The sulphuric acid used is freed from arsenic by adding 1 per cent. of nitric acid and distilling. In some experiments, using a pure solution of arsenious acid, no deposit could be obtained in the Marsh tube, although the escaping gases gave a stain on mercuric chloride paper.

W. P. S.

**Two Possible Causes of Discrepancy in Arsenic Analysis.** By A. J. MURPHY (*J. Soc. Chem. Ind.*, 1902, 21, 957—958).—The writer states that the sensitiveness of the sulphuric acid employed in the Marsh-Berzelius test varies from day to day, and that the longer it is exposed to atmospheric oxygen the less sensitive it becomes. Another source of error is that when arsenic is present in both the -ic and -ous forms, the deposit appears more slowly than usual. The remedies are to prepare fresh standards frequently and to allow a blank to run the same length of time as the apparatus containing the arsenical substance.

W. P. S.

**Gosio's Biological Method for the Detection of Arsenic and the Formation of Organic Arsenic, Selenium, and Tellurium Compounds by the Action of Fungi and Bacteria.** By ALBERT MAASSEN (*Chem. Centr.*, 1902, i, 1245—1246; from *Arb. Kais. Ges.-A.*, 18, 475—489. Compare Gosio, *Abstr.*, 1897, ii, 381; Abba, *Centr. Bakt. Par.*, ii, 4, 806; Morpurgo and Brunner, *Oesterr. Apoth.-Zeit.*, [ii], 1, 167; Schmidt, *Diss. Erlangen*, 1899; Abel and Buttenberg, *Abstr.*, 1900, ii, 299).—The solid compounds of selenium and tellurium are attacked by *Penicillium brevicaulis*, forming volatile substances. The volatile selenium compound has a mercaptan-like odour, quite distinct from that of the arsenic compound, but cultures containing tellurium emit an odour resembling that of garlic. The test is best made by adding the sterilised aqueous solutions of the selenium or tellurium compounds to the sterilised nutritive medium. The sulphides and other insoluble compounds of selenium and tellurium, as well as the elements themselves, are not attacked by this mould, or only to a very slight extent after a great length of time, and in this respect these non-metals differ from arsenic. Selenium and tellurium compounds, on the other hand, are attacked by many fungi which do not affect arsenic derivatives. The volatile selenium and tellurium compounds are absorbed by a solution of mercuric chloride with separation of crystals (compare Biginelli, *Abstr.*, 1901, i, 20). Whilst in the animal organism selenium and tellurium compounds are converted into ethyl derivatives, in microbes, methyl derivatives are formed. The reducing property of the cells of animals and microbes is due to the presence of a substance which can exercise this power even when removed from the tissues, but the formation of methyl or ethyl derivatives seems, however, to be really dependent on vital processes occurring only in the organism.

The value of Gosio's test is scarcely affected by these results, since

selenium and tellurium compounds are very rarely met with, and a confirmatory test may be easily made with a microbic culture which attacks selenium and tellurium derivatives but not arsenic compounds.

E. W. W.

**Titration of Free Alkali in Presence of Nitrites.** By KURT ARNDT (*Zeit. anal. Chem.*, 1902, 41, 359—362).—At low temperatures, free ammonia can be titrated by standard acid in presence of the nitrites of ammonium or the alkali metals, using an aqueous solution of aurin as indicator. Carbonates must first be removed by barium chloride, and, in presence of barium, hydrochloric acid should be used for the titration. Litmus and methyl-orange may also be used, but the end reaction is sharpest with aurin.

M. J. S.

**Action of Carbon Dioxide on the Borates of Barium.** By LOUIS CLEVELAND JONES (*Amer. J. Sci.*, 1902, [iv], 14, 49—56. Compare Abstr., 1898, ii, 640).—On passing a current of carbon dioxide through an aqueous, or alcoholic, solution of barium hydroxide containing barium metaborate, the latter is decomposed with formation of boric acid. On evaporating the liquid, a portion of the acid is volatilised, and a further amount is lost when the residue is heated at a high temperature to effect the formation of the barium metaborate. The action of boric acid on barium carbonate is but very incomplete, even at 350°, and, owing to the action of hydrated barium metaborate on barium carbonate at more elevated temperatures, there is no certainty that the residue will have a definite composition. From this it follows that the process originally proposed by Morse and Burton (Abstr., 1888, 755) cannot be recommended for the estimation of boric acid.

L. DE K.

**Analysis of Lithopone.** By CH. COFFIGNIER (*Bull. Soc. Chim.*, 1902, [iii], 27, 829—832).—The author shows that lithopone, which consists chiefly of zinc sulphide, zinc oxide, and barium sulphate, also often contains soluble zinc salts which have no value as paints. In determining the commercial value of lithopone, therefore, it is necessary to estimate the amount of zinc oxide and of the total amount of zinc in a sample after extracting with warm water.

A. F.

**Micrometric Assay of Gold Minerals.** By GUERREAU (*Bull. Soc. Chim.*, 1902, [iii], 27, 790—792).—In some cases of gold assay, the amount of gold obtained is so small as to be scarcely appreciable on the balance. In such cases, it has been proposed to measure the diameter of the gold grain, rendered spherical by fusion in a boric acid bead, by means of a microscope and micrometer eye-piece, and calculate from this the weight of the gold. The author's experiments confirm the accuracy of the method.

A. F.

**Estimation of Albuminoid and Proteid Ammonia.** By LUDWIG W. WINKLER (*Zeit. anal. Chem.*, 1902, 41, 290—300).—The following process is proposed as an improvement on that of Wanklyn for the estimation of the nitrogenous organic impurities in natural waters. To 100 c.c. of the water there are added 5 c.c. of  $N/5$  sul-

phuric acid (or sufficient to produce an acid reaction), and 5 c.c. of a 1 per cent. solution of purified potassium persulphate. The flask is immersed in the steam from a water-bath for 15 minutes, and then thoroughly cooled. The contents are then transferred to a cylinder, and 5 c.c. of the author's modified Nessler reagent containing alkali tartrate (Abstr., 1899, ii, 805) are added drop by drop. For purposes of comparison, 100 c.c. of the same water are treated in the cold with the same quantities of sulphuric acid, modified Nessler reagent, and persulphate, and then sufficient of a standard ammonium chloride solution (1 c.c. = 0.1 mgm.  $\text{NH}_3$ ) to give the same intensity of colour as in the heated sample. This mode of procedure eliminates the correction for the ammonia in the water and reagents. Urea, uric and hippuric acids yield considerably more ammonia by this process than by distillation with alkaline permanganate, but caffeine, leucine, tyrosine, aspartic acid, gelatin, and albumin yield approximately the same amount by both processes. Special experiments with these compounds show that the results are independent of the dilution. It is suggested that the designation "proteid ammonia" should be reserved for that estimated by oxidation with persulphate. M. J. S.

**Detection of the Principal Impurities of Anthracene.** By THEODOR H. BEHRENS (*Rec. trav. chim.*, 1902, 21, 252—253. Compare Abstr., 1901, ii, 351).—The presence of carbazole is detected by making a cold extract of the anthracene with ethyl acetate, allowing the solution to evaporate, redissolving the residue in a few drops of the same solvent, and evaporating on a watch-glass; the carbazole accumulates at the edge of the deposit, and on mixing a small portion with a drop of nitrobenzene containing a few crystals of phenanthraquinone, copper-coloured plates are formed, even when only 0.5 per cent. of this impurity is present. For the detection of phenanthrene, the anthracene is extracted with benzene, the reagent being  $\alpha$ -dinitrophenanthraquinone dissolved in nitrobenzene. In this case, mixed crystals are obtained having the form and colour of the brown needles of the phenanthrene compound but containing a large quantity of anthracene. A. F.

**Estimation of Chloroform Vapour in Air.** By AUGUSTUS D. WALLER (*Proc. Physiol. Soc.*, 1902; *J. Physiol.*, 28, xxxv—xxxvi).—A bottle filled with the mixture of air and chloroform vapour is connected with a water manometer and with a small pipette by which 5 c.c. of olive oil can be discharged into the bottle. This rapidly absorbs the vapour, and at the end of two minutes the percentage of chloroform is directly read on the manometer, which is empirically graduated. In some experiments, the water in the manometer was replaced with paraffin oil. The numbers obtained show that the results are remarkably accurate. W. D. H.

**Soltzien's Method for the Estimation of Sugar.** By K. SCHUMANN (*Chem. Zeit.*, 1902, 26, 605).—The author having tried Soltzien's process (Abstr., 1901, ii, 286), states that the results are in excess of the truth. Cuprous oxide may be completely converted into copper oxide by ignition with or without the aid of nitric acid; sulphuric acid should not be added. L. DE K.

**Detection of Wood-fibre.** By J. HERTKORN (*Chem. Zeit.*, 1902, 26, 632).—Amylsulphuric acid (this vol., ii, 434) is not the only colour test for wood-fibre, as the other alkyl compounds, and particularly the aromatic sulphonic acids, possess this power in a high degree. Ethylsulphuric and benzenesulphonic acids containing a little free sulphuric acid give blue, bluish-green, green, and greenish-yellow colorations on wood-fibre, according to the excess of free acid or the dilution. Naphthalenesulphonic acids cause a deep indigo-blue tinge, whilst the anthracenesulphonic acids and their oxidation products yield deep red colours which, if the liquid is diluted or somewhat neutralised, are orange or yellow. If aromatic hydrocarbons are heated with strong sulphuric acid until sulphur dioxide is given off, the reagent gives the most intense red or blue colours with wood-fibre, but, at the same time, the cellular fibre (Zellstoff) is also somewhat affected.

L. DE K.

**Estimation of Colophony in the Presence of Fatty Acids.** By D. HOLDE (*Zeit. angew. Chem.*, 1902, 15, 650—657).—A combination of the methods of Twitchell and Gladding. The fat or soap is fully saponified with alcoholic potassium hydroxide. The resulting soap freed from alcohol is, if necessary, separated from unsaponifiable matter by extraction with benzene, and then decomposed by means of hydrochloric acid. The fatty and resinous acids are removed from the liquid by repeatedly agitating it with ether, and this is then evaporated. The residue is now dissolved in absolute alcohol and treated with a current of hydrogen chloride; the product is boiled with water and dissolved in ether. The aqueous layer is neutralised and evaporated, when it is again acidified and repeatedly extracted with ether. The united ethereal solutions are shaken with aqueous potassium hydroxide containing 10 per cent. of alcohol, and the ether is then alternately shaken with water and alkali. The resin is now isolated from the mixed alkaline solutions by acidifying with hydrochloric acid and agitating with ether, which, on evaporation, leaves the resin in a fairly pure state. Traces of adhering fatty acids are now removed by Gladding's silver method. Colophony may be assumed to contain 8 per cent. of unsaponifiable matter, so a correction should be applied when calculating the percentage of resin. The process may also be used for the estimation of resin in the alcoholic extract of ceresin or paraffin.

L. DE K.

**Osmotic Analysis of Urine.** By ANTON STEYERER (*Beitr. chem., Physiol. Path.*, 1902, 2, 312—335).—Numerous analyses of the urine are given under normal conditions, and under the influence of certain drugs and of certain diseases. The main object of the paper is to insist on the importance of 'osmotic analysis' for diagnostic purposes. Among the pathological conditions described are three cases in which one ureter was compressed by new growths. In all three cases there was a great decrease of the molecular concentration of the urine.

W. D. H.

**Jolles' Method of Estimating Uric Acid in Urine.** By E. RICHTER (*Zeit. anal. Chem.*, 1902, 41, 350—359).—Of the three

methods in use for estimating uric acid in urine, namely, those of Ludwig-Salkowski, Hopkins-Folin, and Jolles (*Abstr.*, 1900, ii, 450), the first gives results about 2 per cent. too low, and the second fails with many pathological urines, and especially with those which contain crystalline deposits of uric acid.

The author confirms the accuracy of Jolles' method by numerous test analyses of pure uric acid, and draws attention to the special precautions necessary for obtaining correct results. The chief of these are (1) that towards the end of the oxidation the permanganate solution should not be added in larger quantities than 6—8 drops at once, although time may be saved if, when the yellow colour produced by that quantity does not disappear in five minutes, the mixture is made up to 500 c.c. and boiled for an hour, 2 c.c. more of permanganate being added during that time; (2) whilst neutralising with soda, the mixture must be thoroughly cooled, especially towards the close; (3) the alkaline mixture must be transferred to the azotometer and analysed immediately, otherwise traces of ammonia will be lost and the accuracy of the result impaired.

M. J. S.

**Estimation of Carbohydrates in Normal Urine by the Schotten-Baumann Method of Benzoylation.** By B. REINOLD (*Pflüger's Archiv*, 1902, 91, 35—70).—The amount of benzoate obtained from normal urine by the Schotten-Baumann method varies greatly with the conditions of the experiment, more especially with the amount of benzoyl chloride used, the amount of sodium hydroxide present, and the previous treatment of the urine with soda or basic lead acetate. The author has been unable to devise any modification of the method by which the same percentage of the total carbohydrate is precipitated from different urines. This process, therefore, when applied to normal urines, does not yield quantitative or even strictly comparable results.

A. H.

**Separation of Ternary Compounds and Bases from Animal or Vegetable Liquids.** By S. DOMBROWSKI (*Compt. rend.*, 1902, 135, 182—184). **Nitrogenous Compounds and Alkaloids of Normal Urine.** By S. DOMBROWSKI (*ibid.*, 244—246).—The experiments were made on urine. Normal lead acetate is added, and various nitrogenous substances are separated from the filtrate by the use of normal mercury acetate. By the use of the method, it is claimed that, among other substances, various alkaloids and mannitol can be separated from normal urine.

W. D. H.

**Blumenthal's Method of Estimating Hippuric Acid.** By FRANZ SOETBEER (*Zeit. physiol. Chem.*, 1902, 35, 536—539).—An examination was made of this method (*Zeit. klin. Med.*, 40, Heft. 3 and 4), and the conclusion drawn that it is untrustworthy. Lewin's results (*ibid.*, 42, Heft. 4 and 5), in which this method was employed, are therefore useless.

W. D. H.

**Estimation of Guanidine.** By A. VOZÁRIK (*Zeit. angew. Chem.*, 1902, 15, 670—672).—Eight grams of the guanidine salt are dissolved

in water and a little ammonia and the solution is diluted to 1 litre. When clear, 25 c.c. are mixed with 100 c.c. of ammonium picrate solution prepared by dissolving 8 grams of ammonium picrate, 0.075 gram of guanidine picrate, and 5 c.c. of ammonia (sp. gr. 0.91) in a litre of water. After 6—12 hours, the precipitate is collected on a Gooch asbestos filter and washed with picrate solution; after removing the adhering liquid as much as possible by suction, the crucible and contents are dried at 110° and weighed. The precipitate retains 1 and the asbestos layer 2.4—2.6 per cent. of its weight of ammonium picrate, for which allowance must be made; 1 mol. of the picrate is equivalent to 1 mol. of guanidine.

L. DE K.

**Microchemical Detection of Alkylamines.** By THEODOR H. BEHRENS (*Zeit. anal. Chem.*, 1902, 41, 269—279).—I. *Diamines: Separation from Monoamines.*—This is readily effected by shaking with benzoyl chloride and excess of sodium hydroxide, thus converting the alkylenediamines into their [dibenzoyl derivatives, which are sparingly soluble in hot water. The product is warmed with water to remove monoamines and ammonia, then dissolved in a little alcohol. Water is added to incipient turbidity, which is removed by warming, and the solution then allowed to crystallise under the microscope. The diamines may also be liberated from their benzoyl derivatives by heating with dilute hydrochloric acid at 160—170° in a sealed tube and distilling with sodium hydroxide. They can then be converted into platinichlorides. This course is the more advisable when trimethylenediamine occurs mixed with tetra- and penta-methylenediamines.

II. *Monoamines. A. Group Separations.*—By distillation with aqueous sodium hydroxide, the primary, secondary, and tertiary amines are separated from the non-volatile tetra-alkyl bases. The residue (1) is acidified with hydrochloric acid, dried, and extracted with chloroform or isobutyl alcohol, in which the chlorides of the quaternary bases are soluble. The distillate (2) is shaken with benzenesulphonic chloride (*Abstr.*, 1892, 64) and excess of sodium hydroxide. The primary amines (including ammonia) are converted into the corresponding benzenesulphonamides, which are soluble in sodium hydroxide, the secondary amines yield insoluble derivatives, and the tertiary are not affected. The reaction is complete in five minutes. The mixture is warmed to decompose excess of benzenesulphonic chloride, then cooled, and left to subside.

(3). After subsidence, the alkaline solution is removed and acidified, and the precipitate obtained is shaken with benzene, which dissolves the derivatives of the primary amines and of ammonia, leaving the tertiary amines in the acid solution (4).

(5). The sediment from (2) containing the secondary amines is washed and extracted with benzene or chloroform.

(6). The benzene solutions (3) and (5) are evaporated in small glass tubes, fuming hydrochloric acid is added, and the sealed tubes are heated for 10 minutes at 160°.

B. *Detection of the Individual Bases.*—The saponified product of A 3 is warmed to expel the acid, neutralised with sodium carbonate, and one-third of it distilled with sodium hydroxide. The distillate is added

to the other two-thirds and the whole again distilled. Ammonia is thus removed. Excess of soda is then added and the amines are distilled over. They are then converted into dinitro- $\alpha$ -naphthoxides, which are easily distinguished by their crystalline forms, or may be partially separated by treatment with oil of turpentine. The secondary amines (A 5) are similarly distilled and converted into dinitronaphthoxides.

The tertiary amines (A 4) are converted into platinichlorides or ferrocyanides, which are examined by the polariscope.

The chlorides of the quaternary bases (A 1) are also converted into platinichlorides or ferrocyanides, but in the case of mixtures the latter give confused crystals.

The microscopic characters of the various crystals, as also those obtained with magnesium acetate and sodium phosphate, uranyl acetate, platinic iodide, platinous chloride, palladium dichloride, and chloroanil, are described in the paper.

M. J. S.

**Estimation of Acid-Albumin in Digestive Mixtures.** By P. B. HAWK and WILLIAM J. GIES (*Amer. J. Physiol.*, 1902, 7, 460—491).—By careful neutralisation, almost all the acid-albumin formed during digestion can be precipitated. Some of the residual portion may be obtained by boiling, but the larger portion remains permanently in solution, apparently because of its hydration into non-coagulable forms. The presence of proteoses and peptone makes no difference.

W. D. H.

**The Use of Serum Precipitants for the Detection of Blood Spots in Forensic Medicine.** By JULES OGIER and HERSCHER (*Ann. Chim. anal.*, 1902, 7, 241—245).—The blood spot is dissolved in water and 2 or 3 c.c. of the solution are put into a test-tube 10—12 cm. long and 4—5 mm. diameter. A number of similar tubes are filled with solutions of blood of apparently the same strength and of various origin, such as blood of human beings, oxen, pigs, sheep, dogs, &c.

After adding to each 10 drops of the serum reagent, the tubes are immersed in water at 37—40°, and in the case of human blood a bulky precipitate will form after about 10 minutes and be fully deposited after half-an-hour. No notice should be taken of any small precipitate forming after that time, as other kinds of blood also gradually precipitate. Old blood spots if they have become insoluble, may also be recognised by this means.

The serum reagent consists of the serum of the blood of rabbits which have been repeatedly subcutaneously injected with the serum of human blood. At a temperature of -5° it may be kept active for about four months.

L. DE K.

**Qualitative Reactions of Reducing and Oxidising Diastases.** By M. EMM. POZZI-ESCOT (*Ann. Chim. anal.*, 1902, 7, 260—262).—When the living tissue of vegetable or animal origin decomposes hydrogen peroxide but does not affect a mixture of hydrogen peroxide with tincture of guaiacum, reductases may be suspected. In this case, they are treated out of contact with the air with solutions of indigo, litmus, or ferric ferri cyanide and any reducing action observed. They



also cause an evolution of hydrogen sulphide when mixed out of contact with air with sulphur and potassium fluoride.

Oxydases may be recognised by the blue colour produced on adding them to an emulsion of water and tincture of guaiacum and exposing to the air. They also reoxidise phenolphthalin to phenolphthalein so easily recognised by alkalis. Greiss' reagent and *m*-phenylenediamine should not be employed. L. DE K.

**Malt Analysis.** By ARTHUR R. LING (*J. Fed. Inst. Brewing*, 1902, 8, 441—454).—A number of estimations of the 'diastatic power' of malt were carried out in order to test the accuracy of Kjeldahl's 'law of proportionality.' It was found that the law does not hold either for green malt or for low-dried malt when their extract is allowed to act on a solution of starch at the ordinary temperature. The 'diastatic power' as usually estimated may be misleading, since in order to meet the requirements of the 'law of proportionality' only very dilute solutions of diastase should be employed.

The following method is recommended for the estimation of extract. The moisture is first estimated. Fifty grams of finely powdered malt are introduced into an Erlenmeyer flask, 400 c.c. of water at 72° are added, the mixture is kept at 65° for an hour, and occasionally shaken. The mash is then cooled and sufficient water added to make the total water present 500 grams. The whole is then mixed and filtered, and the sp. gr. of the filtrate is determined. The volume (*V*) occupied by the dissolved matter from 50 grams of malt can then be calculated by means of the formula  $V = \frac{100S(500 + W)}{15.9(D - 10S)}$ , in which *S* is the number of grams of dissolved matter in 100 c.c. of wort, *W* the weight of water in 50 grams of malt, and *D* the sp. gr. of the wort (water = 1000).

E. G.

[Choline as a Criterion for Artificial Brandy.] By HEINRICH STRUYE (*Zeit. anal. Chem.*, 1902, 41, 284—289).—The author considers that the presence of choline may be employed as a criterion of an artificial brandy, as that substance is never found in genuine brandy, but exists in the flavouring ingredients which are added to commercial alcohol to simulate the natural spirit. The choline is detected by Florence's reaction (*Abstr.*, 1900, ii, 328). The aqueous residue obtained by distilling off the alcohol from 50 c.c. of the brandy is mixed with a few drops of dilute sulphuric acid, then with an excess of calcium hydroxide, and dried. The dry residue is extracted with 97 per cent. alcohol and the extract evaporated to dryness, then redissolved in a few drops of water and dried on a microscope slip. A drop of Florence's iodine solution is added and the preparation examined for the characteristic iodocholine crystals. M. J. S.

## General and Physical Chemistry.

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**Effect of the Presence of Hydrogen on the Intensity of the Lines of the Carbon Spectrum.** By ARTHUR M. HERBERT (*Phil. Mag.*, 1902, [vi], 4, 202—207).—When an induction spark is passed through mixtures of carbon dioxide and hydrogen under atmospheric pressure, it is found that the intensity of the strong red line of the carbon spectrum rapidly diminishes with increasing percentage of hydrogen, far more rapidly than the strong violet line of the carbon spectrum under the same conditions. In a mixture with 5 per cent. of hydrogen, the red lines of the carbon and hydrogen spectra are about equally strong; in a mixture with 50 per cent. of hydrogen, the red carbon line is scarcely visible. The violet carbon line, on the other hand, is quite distinct in a mixture with 90 per cent. of hydrogen. Similar results are obtained when carbon monoxide or coal gas is substituted for carbon dioxide. When, on the other hand, the carbon compounds are diluted with air, the intensities of the two carbon lines diminish more or less equally. Special experiments show that the rapid extinction of the red carbon line in presence of hydrogen is not an apparent effect due to the glare of the neighbouring red hydrogen line. It is suggested that the red and violet lines belong to different carbon spectra, and that the molecular combination which gives rise to the red line is destroyed by hydrogen. J. C. P.

**Spectra of Potassium, Rubidium, and Cæsium, and their Mutual Relations.** By HUGH RAMAGE (*Proc. Roy. Soc.*, 1902, 70, 303—312. Compare this vol., ii, 545).—The oxyhydrogen flame spectra of these metals have been studied, and the lines observed, along with those already known, have been sorted into three series (a principal, and a first and second subordinate series). Diagrams, in which oscillation frequencies are taken as abscissæ, and either (1) the atomic masses, or (2) the squares of the atomic masses, as ordinates, have been drawn, and these show the close connection between the spectra and the atomic masses. Empirical formulæ are given by which the two subordinate series can be calculated with considerable accuracy, and the two limits in each spectrum towards which the two subordinate series converge have been determined. These formulæ show that the differences in the corresponding series depend wholly on the atomic masses of the elements. J. C. P.

**Deviabale Rays of Radioactive Substances.** By E. RUTHERFORD and A. G. GRIER (*Phil. Mag.*, 1902, [vi], 4, 315—330).—Uranium, thorium, and radium emit both deviable and non-deviable rays, the proportion of deviable rays being largest in the case of uranium; polonium, on the other hand, gives out no deviable rays. The active products separated from uranium and thorium contain all the substance responsible for the deviable rays, whilst the original radioactive material still retains the power of emitting, in the case of uranium a

large proportion, and in the case of thorium 30 per cent., of the non-deviable rays. The authors think that most of the deviable rays from uranium and thorium may be given out by a secondary product, derived by disintegration from the uranium or thorium molecule; the difference in properties between these secondary products (uranium X and thorium X) and the original substances renders their separation possible. The non-deviable rays may be due to the other secondary product, or to an inductive action of  $\text{UrX}$  or  $\text{ThX}$  on the mass of the radioactive material.

J. C. P.

**Amalgam Potentials, and the Question whether Metals Dissolved in Mercury are Monoatomic.** By FRITZ HABER (*Zeit. physikal. Chem.*, 1902, 41, 399—406).—Meyer's proof (Abstr., 1891, 984) that certain metals dissolve in mercury in the atomic form is regarded as invalid, since the metals may dissolve, not as such, but in the form of mercury compounds. If the compound formed be represented generally as  $\text{Hg}_m\text{M}_n$ , then Meyer has proved  $n=1$ , but assumed  $m=0$ . The author deduces a new expression for the *E.M.F.* of an amalgam concentration cell, based on the supposition that a compound  $\text{Hg}_m\text{M}_n$  is formed, which dissolves in excess of mercury. This expression is applicable in the two particular cases studied by Meyer (*loc. cit.*) and von Tülin (Abstr., 1890, 1046), and is analogous to the formula obtained by Dolezalek for the potential difference of two accumulators containing dilute sulphuric acid of different concentration.

J. C. P.

**The Potentials of Alloys and the Formation of Superficial Layers, being an Addition to the Paper on the Disintegration and Pulverisation of Cathodes.** By FRITZ HABER (*Zeit. Elektrochem.*, 1902, 8, 541—582).—In a former paper (this vol., ii, 441), it was shown that there are two kinds of alloys of sodium with lead or tin. Those containing small quantities of sodium evolve hydrogen slowly when placed in contact with water, and in a solution of lithium chloride in methyl alcohol at  $-8^\circ$  show the same potential as lead. Those containing more sodium are pulverised in contact with water and show a higher potential. It is now shown that the low potential of the less concentrated alloys is due to the formation of a superficial layer of lead (or tin) in contact with the cold liquid, the alloy then behaving as if it consisted of lead (or tin). In contact with a concentrated solution of sodium hydroxide at the ordinary temperature, this does not occur, the potential being much higher. Alloys of other metals which form compounds exhibit analogous phenomena: for example, the alloys of zinc and copper containing more copper than corresponds with the formula  $\text{Zn}_2\text{Cu}$  have the same potential as copper. Frozen sodium amalgam also behaves in this way, for a similar reason.

The potentials of the alloys rise in steps which appear to correspond with (a) pure lead, (b) a mixture of Pb and  $\text{PbNa}_x$  which decomposes water slowly, (c) a mixture of  $\text{PbNa}_x$  and  $\text{PbNa}_y$  (the latter compound exhibits the phenomenon of pulverisation) and (d) pure sodium. The values of  $x$  and  $y$  are not known. The tin alloys are quite similar to those of lead.

T. E.

**Transmission of Galvanic Polarisation through Platinum and Palladium Plates.** By WALTHER NERNST and A. LESSING (*Chem. Centr.*, 1902, ii, 240—241; from *Nachr. k. Ges. Wiss. Göttingen*, 1902, 146—159).—Root's experiments on the diffusion of hydrogen through platinum have been repeated and experiments have also been made with a small, sealed, platinum test-tube, the surface of which was platinised where it was in contact with dilute sulphuric acid. The potential difference between the inner surface and the liquid was first measured; the outer wall was then polarised and the potential inside and outside again determined. According to Zermelo, if the phenomenon is one of diffusion then the time required for the concentration (potential) of the hydrogen to attain a certain value on the other side of the plate is proportional to the square of the thickness of the plate. The results showed that in the case of hydrogen and oxygen the phenomenon is not due to diffusion but rather to the passage of electricity through pores contained in the platinum plates. It was found impossible, however, to obtain direct evidence of the presence of these pores. On the other hand, the passage of hydrogen through palladium follows Zermelo's law. Oxygen does not diffuse; the action of the oxygen liberated at the anode or of an oxidising agent depends on the destruction of the hydrogen potential on the other side of the plate. The diffusion phenomenon is independent of the source from which the hydrogen is obtained or of the method of its preparation. The concentration of hydrogen on one side of the plate is not affected by passing hydrogen through the liquid on the other or by adding a reducing agent such as potassium cobalticyanide.

E. W. W.

**Electrical Conductivities of Solutions in Ethyl Bromide.** By WLADIMIR A. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 466—472).—The author has made measurements, by the Kohlrausch-Ostwald method, of the electrical conductivities of various solutions of aluminium tribromide and of the compound  $\text{AlBr}_3 \cdot \text{EtBr} \cdot \text{Br}_2 \cdot \text{CS}_2$ ; the conductivities of these solutions are less than those of aqueous solutions of the normal salts. The molecular conductivity of the aluminium tribromide solution diminishes considerably as the dilution increases. With the complex compound, however, this change with dilution is but small.

Metallic aluminium is deposited on the cathode when aluminium bromide in ethyl bromide solution is subjected to electrolysis, but the complex compound referred to above cannot be electrolysed.

T. H. P.

**Galvanic Cells and the Phase Rule.** By W. REINDERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 5, 182—193).—The case mainly discussed by the author is that in which the electrolyte contains two different metallic salts,  $\text{M}_1\text{Z}$  and  $\text{M}_2\text{Z}$ , and the electrode may consist of one or both of the metals  $\text{M}_1$  and  $\text{M}_2$ . The possibility of the two metals forming a homogeneous liquid or solid solution or a compound is taken into account. The paper is a theoretical one and not suitable for abstraction.

J. C. P.

**Asymmetry of the Electrocapillary Curve.** By JOHANNES JACOBUS VAN LAAR (*Zeit. physikal. Chem.*, 1902, 41, 385—398. Compare Palmaer, Abstr., 1898, ii, 276; 1899, ii, 347; 1901, ii, 370; Smith, Abstr., 1900, ii, 330).—A theoretical discussion of the capillary electrometer. The electrocapillary curve consists of two distinct portions of a parabolic nature, which cut each other at zero potential. There is a maximum point on the ascending curve, but this maximum need not correspond with zero potential. It follows that Lippmann's capillary electrometer cannot be used for the direct determination of potential differences between metal and electrolyte. J. C. P.

**Electrolysis of Molten Salts.** By GUIDO BODLANDER (*Zeit. anorg. Chem.*, 1902, 32, 235—238).—A reply to Lorenz (this vol., ii, 591) with reference to the work of Suchy (Abstr., 1901, ii, 369). The author has considered the cell studied by Suchy from a thermodynamic point of view and finds that this leads to a conclusion opposite to that experimentally found. J. McC.

**Electrolysis of Molten Salts.** By RICHARD LORENZ (*Zeit. anorg. Chem.*, 1902, 32, 239—246).—Polemical—a reply to Bodlander (see preceding abstract). The author justifies the methods used by Suchy (Abstr., 1901, ii, 369) in obtaining his results. J. McC.

**Electrochemical Behaviour of Sulphur.** By FRIEDRICH WILHELM KUSTER (*Zeit. Elektrochem.*, 1902, 8, 496—499).—The author has observed that during the electrolysis of a solution of a polysulphide both the current and the voltage undergo periodic variations, which are shown to be due to the deposition of sulphur on the anode. The periodicity of the phenomenon is, however, difficult to understand. In order to throw light on this, a number of measurements of the potential differences between electrodes of platinum or of silver and solutions of sodium polysulphides are made. The results show that such electrodes may be regarded as sulphur electrodes, just as a platinum plate saturated with oxygen may be regarded as an oxygen electrode. T. E.

**Laws of Electrolysis of the Vapours of Alkali Salt.** By HAROLD A. WILSON (*Phil. Mag.*, 1902, [vi], 4, 207—214. Compare Abstr., 1899, ii, 722; 1901, ii, 490).—When a salt solution is sprayed, and the vapour of the salt is caused to pass between two electrodes at 1350°, the quantity of vapour and the amount of electricity transported by it are proportional. Further, when a definite amount of any salt passes between the electrodes, the saturation current is inversely proportional to the chemical equivalent of the salt, and the factor of proportionality is the same as in the case of aqueous electrolytes. These results demonstrate the complete analogy between vapours of salt and electrolytes, so far as the passage of a current is concerned. J. C. P.

**Electrolysis of Alkali Chlorides with Platinised Electrodes.** By FRITZ FOERSTER and ERICH MULLER (*Zeit. Elektrochem.*, 1902, 8, 515—540).—The authors confirm the observation made by Lorenz and

Wehrlin (Abstr., 1900, ii, 476) that the *E.M.F.* required to electrolyse a solution of sodium chloride with a platinised anode is approximately 0.5 volt less than that required with a smooth platinum anode, but show that the only difference in the chemical behaviour of such anodes is that at the platinised anode oxygen and chlorate begin to be formed somewhat later and at a higher concentration of the hypochlorite than is the case at a smooth anode; thereafter the two behave similarly.

Chemical experiments show that platinum black decomposes hypochlorous acid into oxygen, and hydrochloric and chloric acids, but that the velocity of the change is far too small to explain the formation of these substances at the anode during electrolysis.

The *P.D.* between a platinised platinum cathode and a concentrated solution of sodium chloride containing a little chromate is constant, for since hypochlorites are not reduced appreciably at such a cathode, it behaves like a normal hydrogen electrode. With a cathode of this kind and a platinised anode, the *E.M.F.* required to electrolyse a solution of sodium chloride is very little greater than that theoretically needed,  $2.23 + cr$ , where 2.23 is the *E.M.F.* needed to decompose sodium chloride,  $c$  the current, and  $r$  the resistance of the solution. With a smooth anode, the *E.M.F.* is higher by a quantity which increases with the duration of the electrolysis to as much as 0.8 to 0.9 volt. A similar difference is found in all cases in which oxygen is evolved at the anode: for example, in the electrolysis of sulphuric acid or sodium hydroxide.

These large differences cannot be explained by differences in the concentration of the solution in contact with the anode. An alkaline solution of potassium iodide (from which no oxygen is evolved during electrolysis) gave a difference of at most 0.07 volt between smooth and platinised anodes.

The authors suggest that the difference may be due to the greater polarisation capacity of the platinised anode, owing to which the concentration of the occluded oxygen in it would be very much smaller than in a smooth anode.

T. E.

### Electromotive Behaviour of Hypochlorous and Chloric Acids.

By ROBERT LUTHER (*Zeit. Elektrochem.*, 1902, 8, 601—604).—The *P.D.* between an indifferent electrode and a solution containing hypochlorous and hydrochloric acids and chlorine may be conditioned by any one of the following equilibria ( $F$  stands for an electric charge),  $2Cl' + 2F \rightleftharpoons Cl_2$ ;  $Cl_2 + 2H_2O + 2F \rightleftharpoons 2HClO + 2H^+$ ;  $2Cl' + H_2O + 4F \rightleftharpoons 2HClO + 2H^+$ .

In a solution containing hydrochloric and hypochlorous acids and chlorine in equilibrium with each other, the ratio  $Cl_2/H^+ \times Cl' \times HClO =$  a constant (Jakowkin, Abstr., 1899, ii, 736), and in such a solution each of the above equilibria would give the same *P.D.* The *P.D.* corresponding with the first is known from the *E.M.F.* of the chlorine-hydrogen cell. The author shows that from these data it is possible to calculate the *P.D.* corresponding with the remaining two equilibria in solutions containing varying quantities of hydrochloric and hypochlorous acids and chlorine. Applying these calculations to Müller's measurements (this vol., ii, 591), he shows that the second equation leads to

impossible or highly improbable concentrations of chlorine in the solutions, whilst the third equilibrium gives concentrations of hydrochloric acid which are approximately proportional to the concentration of the hypochlorous acid used. It is therefore probable that the *P.D.* of a platinum electrode immersed in a solution of hypochlorous acid is conditioned by the equilibrium  $2Cl' + H_2O + 4F \rightleftharpoons 2HClO + 2H\cdot$ . T. E.

**The Behaviour of Hypochlorous Acid and its Salts during Electrolysis.** By FRITZ FOERSTER and ERICH MÜLLER (*Zeit. Elektrochem.*, 1902, 8, 633—638 and 665—672).—Measurements of the discharge potential show that, in solutions of equal concentration, ClO ions are discharged at a somewhat higher potential than OH ions, the discharge potential of Cl ions in neutral solution being still higher. When a solution of hypochlorous acid, acidified with phosphoric acid, is electrolysed, oxygen and chlorine are evolved at the anode and chloric acid formed there. This is most simply explained by assuming that ClO ions are discharged and then react with water as follows,  $6ClO + 3H_2O = 2HClO_3 + 4HCl + 3O$ . The Cl ions thus formed are discharged at once, giving chlorine gas. The quantities of the products found are in good agreement with this view. In neutral or alkaline solutions of hypochlorites, the same reaction appears to take place; chlorine is not evolved as gas, however, but is found in the solution as chloride, which takes part in the further electrolysis.

T. E.

**Cuprous Compounds.** By GUIDO BODLANDER (*Zeit. Elektrochem.*, 1902, 8, 514—515).—The cuprous ion has the formula  $Cu^+$ , not  $Cu_2^{++}$ . The electrolytic potential (Abstr., 1901, ii, 2) of cuprous copper is  $-0.454$  volt. The solubility products of the cuprous halogen salts are,  $1.2 \times 10^{-6}$  for  $CuCl$ ,  $4.15 \times 10^{-8}$  for  $CuBr$ , and  $5.06 \times 10^{-12}$  for  $CuI$ . The tendency to form complex ions such as  $CuCl_2'$  is measured by the equilibrium constant  $k = (CuCl_2') / (Cu')(Cl')^2$ . The value of  $k$ , is  $3.95 \times 10^4$  for the ion  $CuCl_2'$ ,  $1.1 \times 10^5$  for  $CuBr_2'$ , and  $1.55 \times 10^8$  for  $CuI_2'$ . The solubility product therefore decreases and the tendency to form a complex ion increases as the discharge potential of the halogen diminishes. This is in accord with the author's theory (Abstr., 1899, ii, 542).

T. E.

**Electrolytic Phenomena at the Common Surface of Two Solvents.** By WILHELM HITTORF (*Ann. Physik.*, 1902, [iv], 9, 243—245. Compare this vol., ii, 58).—The author does not agree with the interpretation of his previous results (*loc. cit.*) given by Nernst and Riesenfeld (*Ann. Physik.*, 1902, 8, 600). It is shown that the transport numbers obtained from a weak gelatin solution of cadmium chloride have the same values as those obtained from an ordinary aqueous solution.

J. C. P.

**Electro-affinity as a Basis for the Systematisation of Inorganic Compounds.** By RICHARD ABEGG and GUIDO BODLANDER (*Amer. Chem. J.*, 1902, 28, 220—228).—A reply to the criticisms of Locke (this vol., ii, 240).

E. G.

**Dissociation of Dibasic Acids.** By RUDOLF WEGSCHEIDER (*Monatsh.*, 1902, 23, 599—668. Compare Noyes, *Abstr.*, 1893, ii, 365, and Smith, *Abstr.*, 1898, ii, 155, 284).—The dissociation constant for the second hydrogen atom of dibasic acids, which has been previously calculated from observations made with the acid salt, may be calculated from the molecular conductivity of those acids which show dibasic dissociation at moderate dilutions.

If  $g_1$  represents the univalent ions and  $g_2$  the bivalent ions, present when 1 gram-mol. is dissolved in the volume  $v$ , then (1)  $K = \frac{g_1(g_1 + 2g_2)}{(1 - g_1 - g_2)v}$  and (2)  $s = \frac{g_2(g_1 + 2g_2)}{g_1v}$ , where  $K$  represents the

dissociation constant for the first hydrogen atom and  $s$  that for the second. The equations by which the velocity of the ion is calculated,  $\lambda\infty = l_K + l_A$  and  $\frac{n}{1-n} = \frac{l_K}{l_A}$ , are equally available for univalent or for

polyvalent ions. In the case of symmetrical dibasic ions, the molecular conductivity is expressed as a function of the concentration and the velocity of the ions, hence (3)  $\mu = g_1\mu\infty + 2g_2(l_K + l_{2A})$ . The velocity of carboxylic ions depends chiefly on the number of atoms in the ion. Of two ions containing an equal number of atoms, that with the greater valency has the greater velocity. The difference in velocity is not proportional to the difference in valency. The value of  $g_2$  is calculated from equations (1) and (3);  $g_2 = \frac{\mu^2 - kv\mu\infty(\mu\infty - \mu)}{[2(l_K + l_{2A}) - \mu\infty](2\mu + kv\mu\infty)}$

and hence  $g_1 = \frac{\mu - 2g_2(l_K + l_{2A})}{\mu\infty}$ .

In the case of unsymmetrical dibasic acids, the dissociation of the first hydrogen atom results in a mixture of two acid ions,  $g_1' + g_1'' = g_1$ , and gives therefore two dissociation constants,  $k' + k'' = k$ ; hence there

Acid.	$10^6 \times s.$	Acid.	$10^6 \times s.$
Diglycollic acid .....	37	$\beta$ -Bromoethylsuccinic acid.....	64
Thiodiglycollic acid .....	33	$\alpha$ -Bromoethylsuccinic ,, .....	36
Dithiodiglycollic ,, .....	52	Maleic ,, .....	8 ?
Thiodiacetic ,, .....	475	Fumaric ,, .....	29
$\alpha$ -Thiodipropionic acid.....	364	Mesaconic ,, .....	9
$\alpha$ -Thiopropionacetic ,, .....	452	$\alpha$ -Hydroxycamphoronic acid .....	13
Suberic ,, .....	3.3 ?	$\alpha$ -Hydroxyisocinchomeronic acid.	2
Azelaic ,, .....	4.3	Papaveric ,, .....	70
Malonic ,, .....	10 ?	3-Nitrophthalic ,, .....	40
Benzylidenemalonic ,, .....	3.2	4-Nitrophthalic ,, .....	40
Dibenzylmalonic ,, .....	19	3:6-Dichlorophthalic ,, .....	280
Chloromalonic ,, .....	194	Uvic ,, .....	53 ?
Malic (active) ,, .....	7.5	Hydroxyterephthalic ,, .....	45
Malic (inactive) ,, .....	5.5	Bromoterephthalic ,, .....	76
<i>d</i> -Tartaric ,, .....	45	Nitroterephthalic ,, .....	200
<i>l</i> -Tartaric ,, .....	42	$\beta$ -Hydroxycamphoronic ,, .....	21
Racemic ,, .....	40	Aconitic ,, .....	35
Chlorosuccinic ,, .....	36	Butenyltricarboxylic ,, .....	22
Bromosuccinic ,, .....	39	1:1:2-Trimethylenetricarboxylic	
Bromopyruvic ,, .....	51	acid .....	41



are two constants,  $s'$  and  $s''$ , for the second stage of the dissociation, which stand to the constant determined in the relation  $s' = 1 + b/b s$  and  $s'' = (1 + b)s$ , where  $b = k'/k''$ .

The values given on the preceding page have been calculated from previously published conductivity experiments, partly of other authors.

The author compares his values for  $s$  with those obtained by Smith (*loc. cit.*), points out some probable sources of error, and concludes that the influence of constitution on the dissociation constant of the second hydrogen atom is not so simple as suggested by Noyes (*loc. cit.*) and Smith.  
G. Y.

**Boiling Point Curve of the System—Hydrazine + Water.** By CORNELIS A. LOBBY DE BRUYN and J. W. DITO (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 5, 171—174).—The boiling points of hydrazine-water mixtures of different composition have been determined, as well as the composition of the vapour given off by the boiling liquid in each case. The boiling point curve shows a maximum at the temperature  $120.5^\circ$  (pressure 771 mm.) for a mixture containing  $58.5 \text{ N}_2\text{H}_4$  to  $41.5 \text{ H}_2\text{O}$ .  
J. C. P.

**Studies in Vapour Composition. II.** By HECTOR R. CARVETH (*J. Physical Chem.*, 1902, 6, 321—338).—A continuation of the author's previous paper (this vol., ii, 600). A simple form of apparatus for heating a system by vapour is described. The author extends his previous discussion to three component and multicomponent systems.  
L. M. J.

**Numerical Studies on The Equation of Fluids. An Expansion Formula for Liquids.** By EDOUARD MALLET and L. FRIDERICH (*Arch. Sci. phys. nat.*, 1902, 14, 50—58).—The formula  $v = c - d \log(t_c - t)$  was proposed by Avenarius for the expansion of liquids,  $t_c$  being the critical temperature. The authors find that if  $t_c$  be replaced by a constant  $A$ , in general a few degrees above the critical temperature, the formula gives results in good accord with the experimental data for temperatures up to  $30^\circ$  or  $40^\circ$  below the critical. The formula permits of the ready calculation of the coefficient of expansion at any temperature and it is found that the ratio of  $c$  to  $d$  is almost constant, only varying, in the 25 compounds considered, between 3.66 and 3.90 with a mean of 3.78.  
L. M. J.

**Physical Purity of Liquids.** By F. V. DWELSHAUVERS-DERY (*Bull. Acad. roy. Belg.*, 1902, 347—349. Compare Traube, this vol., ii, 557).—A chemically pure liquid consists of (a) liquidogenic molecules, (b) gasogenic molecules, (c) molecules of dissolved extraneous gases, especially air, the relative proportions of these constituents depending on the temperature of the liquid. The realisation of a physically pure liquid, that is, one consisting of liquidogenic molecules, only, could not take place, as Traube has suggested (*loc. cit.*), at absolute zero, since solidification would occur and it is doubtful whether this condition was secured by Donny (*Mem. Acad. roy. Belg.*,

1845, 15) who eliminated extraneous gases from water by slow ebullition in a vacuum. T. A. H.

**Formation of Hydrates in Aqueous Solutions.** By OTTO SCHMATOLLA (*Chem. Centr.*, 1902, ii, 495; from *Apoth.-Zeit.*, 17, 490—491).—The change of volume which occurs when alcohol and water are mixed has been measured by adding small quantities of water (3—10 c.c.) to a litre of absolute alcohol, and determining the density of the mixture after each addition. The result showed that up to 25 per cent. alcohol there is a contraction, but on further dilution the volume gradually increases. The curve obtained from the experimental data shows numerous breaks in continuity, especially between 100 and 70 per cent. alcohol, these points corresponding with hydrates containing  $1/16$ ,  $1/8$ ,  $1/3$ , and  $1\text{H}_2\text{O}$ . The transition from contraction to expansion of volume, however, shows no break in continuity of the curve.

When alcohol is diluted with water, two processes take place, (1) the incorporation of the freshly added solvent, and (2) the gradual coalescence of both the lowest compounds of the dissolved substance with the solvent to form more complex compounds. E. W. W.

**Solubility of Sulphur Dioxide in Aqueous Salt Solutions and its Interaction with the Salts.** By CHARLES J. J. FOX (*Zeit. physikal. Chem.*, 1902, 41, 458—482).—In some cases, sulphur dioxide is more soluble in salt solutions than in pure water, in other cases less soluble, the alteration of solubility being nearly proportional to the salt concentration. The solubility increases from sulphate to iodide in the series—sulphate, nitrate, chloride, bromide, thiocyanate, and iodide, and from cadmium to ammonium in the series—cadmium, sodium, potassium, and ammonium. The determination of the temperature coefficient of the solubility shows that all the salts except the sulphates form complexes containing  $\text{SO}_2$ , apparently of the type  $\text{MX} \cdot \text{SO}_2$  (compare Péchard, *Abstr.*, 1900, ii, 398). These conclusions are borne out by the relative conductivities of the salt solutions with and without sulphur dioxide. The conductivity in the case of salts which react with sulphur dioxide is much reduced, owing doubtless to the formation of complex anions with low mobility. Potassium iodide, bromide, chloride, and thiocyanate absorb sulphur dioxide at the ordinary temperature and pressure to form the compounds  $\text{KX} \cdot \text{SO}_2$ . The compound  $\text{KNO}_3 \cdot \text{SO}_2$ , on the other hand, appears to have at the ordinary temperature a dissociation pressure greater than 760 mm., and cannot therefore be obtained under the same conditions as the other compounds. J. C. P.

**Double Salts in Solution.** By P. N. EVANS (*Chem. News*, 1902, 86 4—5).—When to a saturated solution of an electrolyte, a second electrolyte is added having an ion in common with the first, separation of the first electrolyte in the solid form does not always take place; thus a solution of barium nitrate does not cause the separation of barium chloride from a saturated solution of the latter. Many instances of such a behaviour are given. It is thought that this

peculiarity is due to the formation of complex negative ions in solution, or, in other words, of double salts; the latter cannot be obtained in the solid form from these solutions, as the condition that the molecular solubility of the double salt should be less than that of either of the constituents is not fulfilled. The molecular solubility (solubility divided by molecular weight) of twelve double salts is given and compared with that of their constituents. K. J. P. O.

**Insoluble Inorganic Compounds in Colloidal Solution.** By CORNELIS A. LOBBY DE BRUYN (*Ber.*, 1902, 35, 3079—3082).—When certain insoluble substances, such as silver chromate, silver chloride, or sulphur, are formed in a gelatin or sugar solution, a clear solution is first obtained from which the precipitate only separates slowly. In the case of sulphur, the solution slowly develops a bluish- or brownish-red colour from a sugar solution; the different colours are attributed to a difference in the size of the sulphur particles. J. McC.

**Molecular Concentration of Solutions containing Albumin and Salts.** By LÉON FREDERICQ (*Bull. Acad. Roy. Belg.*, 1902, 437—444).—When a crystalloid is added to an aqueous solution of albumin, cryoscopic measurements show that the mixture behaves as if the molecules of the crystalloid were distributed in the volume of the water contained in the solution. The observations were made on aqueous solutions of egg-albumin; the crystalloids employed being sodium nitrate, sodium chloride, and carbamide. It is pointed out that the molecular concentration of solutions is expressed as gram-molecules per litre of solution (Arrhenius), or as gram-molecules added to 1000 grams of water (Raoult), which leads in the case of concentrated solutions to different values for their molecular concentration. T. A. H.

**Rate of Coagulation of Colloidal Silicic Acid.** By WALTER FLEMMING (*Zeit. physikal. Chem.*, 1902, 41, 427—457).—Colloidal silicic acid was obtained by mixing solutions of water glass and hydrochloric acid, and coagulation was regarded as complete when the containing vessel could be inverted, or when the mixture ceased to drop; for the latter method, an apparatus was devised to register the intervals of time between successive drops. The rate of coagulation increases with rising temperature and with increasing concentration of the silicic acid. Hydrogen and hydroxyl ions have a catalytic effect on the rate of coagulation; as the concentration of hydrogen ions increases, the coagulation is first retarded and then accelerated; as the concentration of hydroxyl ions increases, the coagulation is first accelerated and then retarded. J. C. P.

**Intramolecular Rearrangement in Halogen-acetanilides, and its Velocity.** By JAN J. BLANKSMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 5, 178—182. Compare this vol., i, 600; Chattaway and Orton, *Proc.*, 1902, 18, 200).—In presence of hydrochloric acid, acetylchloroanilide is gradually transformed into *p*-chloroacetanilide, and since only the former of the two compounds liberates iodine from potassium iodide, the course of the trans-

formation may be followed quantitatively. The reaction was carried out in 20 per cent. acetic acid solution at 25°, and the velocity constant was found to be that for a unimolecular reaction, whence it follows that the transformation consists in an intramolecular rearrangement of atoms (compare the case of the bromoamides studied by van Dam and Aberson, Abstr., 1901, ii, 88). When double the quantity of hydrochloric acid is added, the velocity constant is nearly four times as great. With sulphuric acid, the conversion takes place very slowly, and the velocity coefficient is not so satisfactorily constant. In glacial acetic acid and alcoholic solutions, the reaction proceeds with increasing velocity owing to the production of a catalyser.

The reaction studied in this paper is much accelerated by light, and it appears to be a general rule that the radicles Br, Cl, NO<sub>2</sub>, NO, and O attached to nitrogen, change places, under the influence of sunlight, with an H atom in the nucleus.

J. C. P.

**Velocity of Decomposition of Bromosuccinic Acid in Aqueous Solution. I. Course of the Reaction at 50°.** By WOLF MÜLLER (*Zeit. physikal. Chem.*, 1902, 41, 483—497).—In aqueous solution, bromosuccinic acid decomposes into hydrogen bromide and either fumaric acid or a mixture of fumaric and malic acids, according to the concentration; the nature, however, of the organic acid produced in the decomposition has no effect on the reaction velocity. In presence of strong acids, the decomposition is retarded, and thus the decomposition is a case of autocatalysis, inasmuch as it is accompanied by an increase of acidity. The author makes the assumption that the reaction velocity is inversely proportional to the concentration of the hydrogen bromide at the time, as well as directly proportional to the concentration of the undecomposed bromosuccinic acid, and it is found that the equation based on this assumption satisfactorily represents the course of the reaction. When a large quantity of strong acid is added to begin with, so large that the increase of acidity during the reaction is relatively negligible, the reaction is unimolecular. The assumption referred to above is in accordance with Euler's theory (Abstr., 1900, ii, 532).

J. C. P.

**Inversion.** By CARL KULLGREN (*Zeit. physikal. Chem.*, 1902, 41, 407—426. Compare Abstr., 1901, ii, 149, 496).—Attempts which have been made to determine the percentage hydrolysis of inorganic salts from the acceleration of sugar inversion induced by these have, in the majority of cases, given a doubtful result, because the inversion coefficient obtained at temperatures near 100° is not constant, but increases rapidly with the time. Even pure solutions of sugar are inverted on prolonged heating at 100° (compare Rayman and Sulč, Abstr., 1897, ii, 136; Smith, Abstr., 1898, ii, 155), and the inversion coefficient rapidly increases. This inversion of pure sugar solutions may be attributed to the hydrogen ions derived from the water itself, from the sucrose (compare Kullgren, Abstr., 1901, ii, 496), and from the invert sugar (compare Cohen, Abstr., 1900, ii, 716). The author proves, however, that only the first stage of the inversion can be quantitatively accounted for in this way; his own numerous experiments show that as the inversion coefficient increases, there is a

formation of acid (apparently from the invert sugar) in gradually increasing quantity, this quantity being nearly proportional to the amount of the invert sugar. On the basis of this observation, the equation  $dx/dt = k.x(A - x)$  is formulated, and it is found that this represents satisfactorily the latter and major part of the inversion process.

As might be expected, there is a similar formation of acid, leading, in most cases, to a rapid increase of the inversion coefficient, when salts are present. With certain highly hydrolysed salts, notably those of aluminium, the inversion coefficient is satisfactorily constant, because the rôle of the acid produced during inversion is insignificant as compared with that of the hydrolysed salt; and, more generally, the smaller the percentage of hydrolysis of the salt, the greater is the relative increase of the inversion coefficient.

J. C. P.

**Synthetic Analysis in Ternary Systems.** By A. W. BROWNE (*J. Physical Chem.*, 1902, 6, 287—312).—It has been shown that the composition of a solid phase separating from a solution may be determined by (1) comparison of the composition of the mother liquor with that of the original solution, and (2) by determining the composition of the solid which can be added to the system without disturbing the equilibrium. The method has been tested in a large number of cases in which the nature of the solid phase varies, and the following systems were investigated. (1) Potassium chloride, hydrogen chloride, and water; solid phase, a pure component, potassium chloride. (2) Sodium sulphate, sodium chloride, and water; solid phase,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , a binary compound of components. (3) Barium chloride, hydrogen chloride, and water; solid phase,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , a binary compound. (4) Ferric chloride, hydrogen chloride, and water; solid phase, hydrated ferric chloride. (5) Potassium sulphate, ammonium sulphate, and water; solid phase, a solid solution of ammonium and potassium sulphates. The graphic method of calculation by the aid of the equilateral diagram was also employed, and the conditions for accurate results are discussed.

L. M. J.

**Formation of Mixed Crystals by Sublimation.** By GIUSEPPE BRUNI and M. PADOA (*Atti R. Accad. Lincei*, 1902, [v], 11, i, 565—569).—The authors have succeeded in obtaining mixed crystals by sublimation, their method of working being as follows. The mixed substances were melted, and the mass afterwards powdered and introduced into a glass tube, which was sealed up after the pressure in it had been reduced to 12—14 mm. of mercury. The tube was then heated in a bath kept at a constant temperature below the melting point of the mixture.

From a mixture of azobenzene and stilbene, mixed crystals were obtained containing a much smaller proportion of stilbene than the original mixture. Mixed crystals were also prepared from mercuric bromide and iodide, the latter being present in smaller proportion than before sublimation.

The relation between the original and final concentrations of the components gives a measure of the distribution-coefficients of the sub-

stances between the heated, solid mixture and the mixed vapour in contact with it.

The crystals formed by sublimation of mercuric chloride and iodide together are mixed crystals, as was pointed out by Selmi in 1844, although the latest text-books state that they are compounds of the compositions  $\text{HgI}_2, \text{HgCl}_2$  and  $\text{HgI}_2, 2\text{HgCl}_2$ . T. H. P.

**Weights of Atoms.** By LORD KELVIN (*Phil. Mag.*, 1902, [vi], 4, 177—198).—A review of the theoretical and experimental work which has been done on the problem of absolute molecular dimensions, and questions connected therewith. The author himself estimates that the number of molecules present in 1 c.c. of a gas is not less than  $10^{20}$ , and is probably greater. On the basis of this value, the weight of one molecule of hydrogen is calculated to be  $0.9 \times 10^{-24}$  gram. J. C. P.

**Mathematical Expression of the Valency Law of the Periodic Table, and the Necessity for Assuming that the Elements of its First Three Groups are Polyvalent.** By GEOFFREY MARTIN (*Chem. News*, 1902, 86, 64—65).—By representing the valencies and the group numbers of the elements on a system of ordinates, the author arrives at the equation,  $v^2 - n^2 - 8(v - n) = 0$ , as giving the law of valency for elements of moderate atomic weight and at the normal temperature, where  $v$  represents the valency and  $n$  the group number. As a result, the elements of the first three groups should be polyvalent, that is, should act with several different degrees of valence towards other radicles. The polyvalent character of these elements is shown in their compounds with metals. K. J. P. O.

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## Inorganic Chemistry.

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**The Hydrates of Perchloric Acid.** By H. J. VAN WYK (*Zeit. anorg. Chem.*, 1902, **32**, 115—120).—The melting point curve of all mixtures of perchloric acid and water has been determined. This has been found to consist of the melting point curves of five hydrates along with the ice curve and the curve for solid perchloric acid. The melting point of perchloric acid is  $-83^{\circ}$ ; that of  $\text{HClO}_4, \text{H}_2\text{O}$  is  $50^{\circ}$ ; that of  $\text{HClO}_4, 2\text{H}_2\text{O}$  is  $-20.6^{\circ}$ ; that of  $\text{HClO}_4, 3\text{H}_2\text{O}$  is  $-47^{\circ}$ ; that of  $\text{HClO}_4, 4\text{H}_2\text{O}$  is  $-40^{\circ}$ ; and that of  $\text{HClO}_4, 6\text{H}_2\text{O}$  is  $-45^{\circ}$ . There also exists a metastable hydrate which melts at  $-64^{\circ}$ . J. McC.

**The Behaviour of Bromine to High Pressure Electric Discharges.** By KARL KELLNER (*Zeit. Elektrochem.*, 1902, **8**, 500—504).—Pure, dry and air-free bromine is enclosed in double-walled tubes, similar to ozone tubes, and submitted to an alternating current at 250,000 to 300,000 volts pressure, obtained by means of a Tesla transformer. After some hours, a sulphur-yellow, crystalline deposit appears on the walls of the tube, and when small quantities of bromine are used the whole may be transformed into the new substance. The author states that the glass itself takes no part in the change. T. E.

**Preparation of Periodates.** By FERDINAND ROQUES and AUGUSTE GERNGROSS (*J. Pharm. Chim.*, 1902, [vi], **16**, 120—121).—Alkali

periodates are readily prepared by the action of an excess of a hypochlorite on an iodide in alkaline solution. Fifty grams of potassium iodide and 20 grams of sodium hydroxide are dissolved in water and a large excess of sodium hypochlorite is added. On heating the mixture on the water-bath, an abundant precipitate of crystalline sodium periodate is gradually deposited. H. R. LE S.

**Liquid Air.** By ARSÈNE D'ARSONVAL (*Ann. Chim. Phys.*, 1902, [vii], 26, 433—460).—An historical summary of the methods devised to prepare liquid air, and an account of experiments carried out by the aid of this product. G. T. M.

**Preparation of Ozone.** By CARL ARNOLD and CURT MENTZEL (*Ber.*, 1902, 35, 2902—2907).—See this vol., ii, 691.

**Ozonic Acid.** By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1902, 35, 3038—3039).—Solid potassium hydroxide is coloured an intense orange-brown by ozone (Wurtz, *Dict. Chim.*, p. 721). The colour is at once destroyed by the addition of water and a vigorous evolution of gas occurs. The coloured substance appears to have no oxidising properties and hydrogen peroxide could not be detected in the aqueous solution. A similar coloration is produced when ozonised oxygen is passed into 40 per cent. aqueous potash cooled by a freezing mixture, but the colour disappears when the solution is removed from the freezing mixture. Rubidium hydroxide behaves in a similar manner, whilst sodium hydroxide is only coloured a faint yellow. It appears probable that the potassium compound is potassium tetra-oxide, and in this case it may be regarded as the salt of an ozonic acid,  $O_3 + H_2O = H_2O_4$ . A. H.

**Amorphous Sulphur.** By ALEXANDER SMITH and WILLIS B. HOLMES (*Ber.*, 1902, 35, 2992—2994).—The solidifying point of molten sulphur depends on the amount of amorphous sulphur, which the sample contains. Thus when 32 grams of amorphous sulphur are dissolved in 100 grams of molten crystalline sulphur, the solidifying point is depressed from  $119.25^\circ$  to  $42.5^\circ$ , a result which, after allowance has been made for the latent heat, would show that the molecule of amorphous sulphur is  $S_8$ . If crystalline sulphur is heated in a sealed tube at  $448^\circ$  for  $1\frac{1}{2}$  hours and then suddenly cooled by ice, about 31 per cent. is converted into the amorphous variety. The proportion of amorphous sulphur formed can be increased by the addition of pyrophosphoric acid or by passing air, sulphur dioxide, or hydrogen chloride through the molten mass; it can be decreased by longer heating, the addition of potassium hydroxide, or by passing nitrogen, carbon dioxide, hydrogen sulphide, or ammonia through the molten mass. The substances, with the exception of carbon dioxide, which have the latter action, will also reduce the amount of any amorphous sulphur previously formed. R. H. P.

**Relations of Sulphur and Iodine, and the Iodides of Sulphur.** By R. W. EMERSON MACIVOR (*Chem. News*, 1902, 86, 5—7. Compare *ibid.*, 1874, 30, 179).—The evidence in favour of the existence



of the compound  $S_2I_2$  is discussed; the author concludes that this compound has not been obtained, and that the blackish-grey material obtained by heating the elements mixed in atomic proportion, which melts at  $66^\circ$ , and not at  $60^\circ$ , is probably a solid solution. K. J. P. O.

**Theory of the Lead Chamber Process.** By FR. RIEDEL (*Zeit. angew. Chem.*, 1902, 15, 858—864).—A reply to Lunge (this vol., ii, 605) and to Haagn (this vol., ii, 604). The author discusses the question of an optimum temperature in the production of sulphuric acid by the lead chamber process. K. J. P. O.

**Formation of Dithionic Acid.** By UBALDO ANTONY (*Gazzetta*, 1902, 32, i, 514—517).—In a paper by Meyer (this vol., ii, 14) on this subject, no mention is made of the work of the author with Lucchesi (Abstr., 1899, ii, 299) and with Manasse (Abstr., 1899, ii, 753). The author's results have anticipated, and are more comprehensive than, those of Meyer. T. H. P.

**Mixed Crystals of Sulphur and Selenium.** By W. E. RINGER (*Zeit. anorg. Chem.*, 1902, 32, 183—218).—An account is given of all the previous work which has been carried out on mixtures of these two elements and the compounds which they have been said to form.

Molten sulphur and molten selenium are miscible in all proportions, but when the atomic percentage of selenium is greater than 10, crystallisation does not take place easily. Even by very slowly cooling, the mixture solidifies in an amorphous form, and when the percentage of selenium is high, crystallisation can only be made complete by heating for many hours near the melting point. The crystalline mixtures probably contain only mixed crystals; no evidence could be found of the formation of a compound. The following melting points of mixtures were determined by the thermometric and dilatometric methods:

Composition in atomic percentage of selenium.	Thermometric.		Dilatometric.	
	Initial m. p.	Final m. p.	Initial m. p.	Final m. p.
0	118.2°	119°	—	—
10	114	116.5	—	—
20	—	114.2	109°	115°
30	—	108	—	—
40	—	106	100	105
50	—	130	108	130
56	—	—	125	135
60	—	136	—	—
65	—	—	137	149
70	—	150	—	—
74	—	—	147	160
80	—	170.5	160	185
85.5	—	—	162	190
90	—	188	175	200
100	217.4	217.8	—	—

These results are given in the form of a melting point curve.

From the molten mixture, three series of mixed crystals may be formed: (a) monoclinic mixed crystals (of the type of monoclinic sulphur) with 0 to 27 atomic percentage of selenium; (b) monoclinic mixed crystals (of the type of the second monoclinic modification of sulphur?) with about 50 to 82 atomic percentage of selenium; and (c) hexagonal-rhombohedral mixed crystals (of the type of metallic selenium) with  $\pm 87$  to 100 atomic per cent. of selenium.

When selenium is added to sulphur, the transition point ( $95.5^\circ$ ) from the monoclinic to the rhombic variety is lowered; when 2.05 atomic per cent. of selenium is present the transition point is  $93.5^\circ$ ; with 4.25 atomic per cent. it is  $91-93^\circ$ ; with 7 atomic per cent. it is  $83-86^\circ$ , and with 12 atomic per cent. it is  $76-82^\circ$ . The mixed crystals of series (a) therefore exhibit the same transition from monoclinic to rhombic crystals below a certain temperature that sulphur does. The mixed crystals of the other two series do not show any transition.

At the ordinary temperature, there exist a series of rhombic crystals with 0 to 10 per cent. of selenium, and the second (extending, however, only from 55—75 atomic per cent. of selenium), and the third series just mentioned.

Selenium dissolves in carbon disulphide only to the extent of one part per thousand, but sulphur-selenium mixtures are so soluble that a solution can be obtained containing up to 1 per cent. of selenium.

J. McC.

**Liquid Hydrosol of Selenium.** By ALEXANDER GUTBIER (*Zeit. anorg. Chem.*, 1902, 32, 106—107).—Liquid hydrosol of selenium has already been obtained by Schultze (*Abstr.*, 1886, 302). The hydrosol can be obtained by reducing selenium dioxide in very dilute solution with hydrazine hydrate; the solution is then dialysed. The hydrosol is a reddish liquid when examined by transmitted light and shows a blue fluorescence in reflected light. Electrolytes cause the precipitation of gelatinous red selenium, which becomes black on heating.

Slow evaporation of the hydrosol over concentrated sulphuric acid at diminished pressure occasionally leads to a solid hydrosol.

The pseudo-solution can also be obtained by reduction with hydroxylamine hydrochloride or hypophosphorous acid, but when so prepared, it does not keep well.

J. McC.

**Tellurium.** By ALEXANDER GUTBIER (*Zeit. anorg. Chem.*, 1902, 32, 31—50. Compare *Abstr.*, 1901, ii, 687).—Crude "36 per cent." tellurium from Selmeczbánya (Hungary) contains, besides tellurium, antimony, copper, bismuth, and iron; "72 per cent." tellurium of the same origin contains zinc, sulphur, silica, and tellurium dioxide as well as the elements mentioned. The substance sold as "purest" tellurium contains only about 95 per cent. of that element. The Hungarian tellurium contains no selenium. The analysis was made by dissolving the dried substance in a mixture of hydrochloric and nitric acids and evaporating to dryness; the residue was dissolved in hot dilute hydrochloric acid and saturated with hydrogen sulphide at  $70-80^\circ$ . The precipitate contained the sulphides of tellurium,

antimony, copper, and bismuth; it was treated with a warm solution of potassium sulphide, and in the filtrate the tellurium was precipitated by hydrazine hydrate (compare *loc. cit.*). The bismuth was separated from the copper by dissolving the precipitate in nitric acid and precipitating as carbonate. The other metals were estimated in the usual way.

The author does not agree with Köthner (this vol., ii, 67) that the best way to obtain tellurium is from the basic nitrate, but recommends the preparation from telluric acid by freeing this from water of crystallisation at a low temperature, converting it into tellurium dioxide, and reducing this in a current of hydrogen. After distilling two or three times in an atmosphere of hydrogen, the tellurium is obtained quite pure in the form of a tin-white metal which can easily be reduced to a grey powder.

Tellurium is dissolved to a very slight extent by methylene iodide; this is not a purely physical action, but is caused by the formation of a small quantity of tellurium iodide which dissolves.

The chemical behaviour of pure tellurium has been examined. In a fine state of division it is not acted on by the oxygen of the air. It dissolves very readily in hot dilute nitric acid and if the proper amount of acid be used it is difficult to precipitate tellurous acid by the addition of water; the nitric acid solution contains no telluric acid. It dissolves in hot concentrated sulphuric acid to a red solution from which tellurium is separated when water is added. If the red solution be boiled for some time, white crystals of pyrotelluryl sulphate,  $2\text{TeO}_2 \cdot \text{SO}_3$ , separate; the crystals dissolve in hydrochloric acid and decompose on heating with water. No compound analogous to  $\text{KCNSe}$  containing tellurium could be obtained. When concentrated solutions of telluric acid and potassium thiocyanate are boiled together, a yellow, amorphous precipitate containing tellurium, carbon, nitrogen, and sulphur is obtained; this substance, however, is not homogeneous.  
J. McC.

**Colloidal Tellurium.** By ALEXANDER GUTBIER (*Zeit. anorg. Chem.*, 1902, 32, 51—54 and 91. Compare this vol., ii, 610).—When a dilute solution of telluric acid (2 to 3 grams per litre) is warmed to about  $50^\circ$  and hydrazine hydrate solution (1:2000) added, a colloidal solution of tellurium is obtained which can be purified in a dialyser. Two modifications of this solution can be formed, a brown and a bluish-green. In reflected light, the solutions show a brown to blue fluorescence, whilst in transmitted light they are clear and transparent. On addition of electrolytes, particularly ammonium chloride, the pseudo-solutions are decomposed. A hydrogel is formed when the solution is boiled or slowly evaporated.

In an additional note, the author states that a pseudo-solution of tellurium can also be obtained from telluric acid by reduction with hydroxylamine hydrochloride, sulphur dioxide, or even by sodium hydrogen sulphite.  
J. McC.

**Compounds of Tellurium and Iodine.** By ALEXANDER GUTBIER and F. FLURY (*Zeit. anorg. Chem.*, 1902, 32, 108—114).—When

tellurium and iodine are fused together in the requisite proportion to form tellurium di-iodide,  $\text{TeI}_2$ , a black substance is produced which possesses a metallic lustre and melts easily. When very carefully heated, it can be sublimed, but its composition does not appear to be constant.

Hydriodic acid acts on telluric acid in two ways. In dilute solution, reduction takes place slowly to tellurium dioxide, and after some time, a dark, granular mass of tellurium tetraiodide,  $\text{TeI}_4$ , separates. No indication could be obtained of the formation of a di-iodide. In concentrated solution, the reaction takes place quickly, and tellurium tetraiodide is at once precipitated as a heavy, iron-grey substance. The tetraiodide is decomposed by water according to the equation:  $\text{TeI}_4 + 2\text{H}_2\text{O} = 4\text{HI} + \text{TeO}_2$ , and a similar decomposition takes place with alcohol. When heated, the tetraiodide melts, but at the same time decomposes. The tetraiodide dissolves in ammonia and alkalis; if dilute hydrochloric acid be added to the clear solution, the whole of the iodine separates and can be estimated by titration with thiosulphate. When the substance is dissolved in dilute sodium hydroxide and then neutralised with dilute sulphuric acid, the addition of excess of silver nitrate precipitates a mixture of silver iodide and silver tellurite; these can be separated quantitatively on account of the solubility of the silver tellurite in ammonia solution, and from the ammoniacal solution the tellurium can be precipitated in the usual way.

J. McC.

**Telluric Acid.** By ALEXANDER GUTBIER and F. FLURY (*Zeit. anorg. Chem.*, 1902, 32, 96—105. Compare Abstr., 1901, ii, 687, and this vol., ii, 558).—When telluric acid is prepared by the process suggested by Staudenmaier (Abstr., 1896, ii, 96), namely, by oxidising a nitric acid solution of tellurium dioxide with chromic acid, dark purple crystals separate if too much chromic acid is used. These crystals are hydrated chromic nitrate,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , and they contain a very small quantity of telluric acid or tellurium nitrate. To obtain pure telluric acid, it is necessary to avoid excess of chromic acid; the telluric acid so obtained is quite colourless. Telluric acid should not be separated from a solution containing sulphuric acid, for the solid substance retains this acid with great tenacity.

When aqueous solutions of telluric acid are evaporated, a turbidity may be produced, but the suspension is so fine that it easily passes through a filter. The telluric acid may, however, separate as a gelatinous, voluminous mass. This substance has been dried in a desiccator and by heating at various temperatures, but no proof could be found of the existence of the telluric acid b,  $\text{H}_2\text{TeO}_4$ , described by Berzelius. The results obtained indicate that, besides telluric acid,  $\text{H}_6\text{TeO}_6$ , and its known easily soluble hydrates, there exist other difficultly soluble hydrates, which all, however, lose water easily when heated, and give tellurium dioxide as the final residue.

J. McC.

**Probable New Oxide of Nitrogen.** By DEMETRIO HELBIG (*Atti R. Accad. Lincei*, 1902, [v], 11, ii, 57).—When a series of electrical discharges is passed through liquid air, a flocculent, greenish

substance is obtained which is very unstable and decomposes at low temperatures with formation of reddish vapours; in some cases, the decomposition is explosive and is accompanied by the evolution of light. All the conditions under which the compound is formed, as also its characters, indicate it to be an oxide of nitrogen, and the author is subjecting it to further study.

T. H. P.

**Hydroxylamine Compounds.** By MAXWELL ADAMS (*Amer. Chem. J.*, 1902, 28, 198—219).—The solubility of hydroxylamine sulphate has been determined with the following results. One gram of an aqueous solution at  $-8^{\circ}$  contains 0.307; at  $0^{\circ}$ , 0.329; at  $10^{\circ}$ , 0.366; at  $20^{\circ}$ , 0.413; at  $30^{\circ}$ , 0.441; at  $40^{\circ}$ , 0.482; at  $50^{\circ}$ , 0.522; at  $60^{\circ}$ , 0.560; and at  $90^{\circ}$ , 0.685 gram of the salt. In the case of hydroxylamine phosphate, 1 gram of an aqueous solution at  $0^{\circ}$  contains 0.012; at  $10^{\circ}$ , 0.015; at  $20^{\circ}$ , 0.019; at  $30^{\circ}$ , 0.027; at  $40^{\circ}$ , 0.040; at  $50^{\circ}$ , 0.055; at  $60^{\circ}$ , 0.077; at  $70^{\circ}$ , 0.102; at  $80^{\circ}$ , 0.133; and at  $90^{\circ}$ , 0.168 gram of the salt.

*Hydroxylamine hydrobromide*,  $\text{NH}_2\cdot\text{OH}\cdot\text{HBr}$ , forms large, white, acicular crystals, and is very soluble in water. *Dihydroxylamine hydrobromide*,  $2\text{NH}_2\cdot\text{OH}\cdot\text{HBr}$ , crystallises in white plates and is readily soluble in water.

The following double salts of mercury and hydroxylamine were prepared and analysed. The *sulphate*,  $\text{HgSO}_4\cdot 2\text{NH}_2\cdot\text{OH}\cdot\text{H}_2\text{O}$ ; the *chloride*,  $\text{HgCl}_2\cdot 2\text{NH}_2\cdot\text{OH}$ , which forms white, acicular crystals, and combines with hydroxylamine hydrochloride with production of the compound  $\text{HgCl}_2\cdot 2\text{NH}_2\cdot\text{OH}\cdot(\text{NH}_2\cdot\text{OH}\cdot\text{HCl})_2$ ; the *chlorides*,

$\text{HgCl}_2\cdot 2\text{NH}_2\cdot\text{OH}\cdot(\text{NH}_2\cdot\text{OH}\cdot\text{HCl})_2$ ,  
 $\text{HgCl}_2\cdot\text{NH}_2\cdot\text{OH}\cdot\text{HCl}$ , and  $2\text{HgCl}_2\cdot[(\text{NH}_2\cdot\text{OH})_2\cdot\text{HCl}]_5$ ; the *bromide*,  
 $\text{HgBr}_2\cdot 2\text{NH}_2\cdot\text{OH}\cdot(\text{NH}_2\cdot\text{OH}\cdot\text{HBr})_2$ .

*Cadmium hydroxylamine bromide*,  $\text{CdBr}_2\cdot 2\text{NH}_2\cdot\text{OH}$ , and *iodide*,  $\text{CdI}_2\cdot 3\text{NH}_2\cdot\text{OH}$ , are also described.

E. G.

**Hydrogen Arsenide.** By LUDWIG VANINO (*Zeit. angew. Chem.*, 1902, 15, 856—858).—An arsenic mirror can be obtained in a Marsh's apparatus when 0.02 gram of arsenious oxide is reduced by pure tin and concentrated hydrochloric acid. In the presence of platinum or copper sulphate, 0.0001 gram of arsenious oxide gives a mirror. Aluminium and dilute hydrochloric acid also reduce white arsenic to hydrogen arsenide, 0.0001 gram of the oxide being recognisable in this way; when iron wire and 20 per cent. hydrochloric acid are used, 0.00005 gram of white arsenic can be found.

The author gives a list of the cases of poisoning by hydrogen arsenide which have been recorded.

K. J. P. O

**Action of Hydrogen Sulphide on Arsenic Acid.** By LE ROY W. McCAY (*J. Amer. Chem. Soc.*, 1902, 24, 661—667. Compare Abstr., 1902, ii, 135).—The author explains the formation of mono-, di-, and tri-thio-oxyarsenic acids when hydrogen sulphide acts on arsenic acid by assuming that the latter can dissociate simultaneously in the two directions shown by the equation  $\text{HO}\cdot + \text{H}_2\text{AsO}_3\cdot = \text{H}_3\text{AsO}_4 = \text{H}_2\text{AsO}_4\cdot + \text{H}\cdot$ , and that the ions produced react with those of

hydrogen sulphide to form monothio-oxyarsenic acid, the ions of which, in turn, form in the same way dithio-oxyarsenic acid, and so on until eventually thioarsenic acid results, but this, being unstable, decomposes into arsenic sulphide and hydrogen sulphide. T. A. H.

**Lecture Experiment: Colloidal Silver.** By FRANZ KUSPERT (*Ber.*, 1902, 35, 2815—2816).—A colloidal solution of silver can be obtained by adding a solution of silver nitrate to a solution of sodium silicate to which formaldehyde has been previously added. The solution, which is quite stable, can be diluted without the precipitation of silver, but it is decomposed by hydrochloric acid, potassium chloride, sodium hydroxide, or hydrogen sulphide. R. H. P.

**The Toning and Fixing of Prints on Silver Chloro-citrate Paper.** By ADOLPHE JOUVE (*Bull. Soc. Chim.*, 1902, [iii], 27, 862—863. Compare this vol., ii, 319).—The author states that in 1898 he published a formula for a combined toning and fixing bath which did not contain any gold; the toning salt was sodium lead thiosulphate in a solution slightly acidified with boric acid. A. F.

**Bleaching Powder.** By HUGO DITZ (*Zeit. angew. Chem.*, 1902, 15, 749—755).—The views expressed by Tiesenholt (Abstr., 1901, ii, 154) on the process of the formation of bleaching powder are not in agreement with the author's experiments (Abstr., 1901, ii, 239). Evidence is brought forward in favour of the view that bleaching powder is not represented by the expression  $\text{CaCl}_2 \cdot \text{Ca}(\text{OCl})_2 \cdot 2\text{H}_2\text{O}$  (Tiesenholt), but that all the chlorine is present in the form of a compound,  $\text{CaCl} \cdot \text{OCl} \cdot \text{H}_2\text{O}$ , or of a compound,  $\text{CaO} \cdot \text{CaCl} \cdot \text{OCl} \cdot \text{H}_2\text{O}$ .

K. J. P. O.

**Solubility of Gypsum.** By GEORGE E. HULETT and LUCIUS E. ALLEN (*J. Amer. Chem. Soc.*, 1902, 24, 667—679).—Determinations of the solubility were made at thirteen temperatures between  $0^\circ$  and  $107^\circ$ , using a pure natural gypsum and distilled water of conductivity less than  $1.5 \times 10^{-6}$ , special precautions being taken to prevent supersaturation (compare Hulett, Abstr., 1901, ii, 493). The following selections from the determinations made show the character of the solubility curve.

Temp.	Gram in 100 c.c. of solution.	Sp. gr. of solution.	Elect. cond. at temp. quoted.
$0^\circ$	0.1760	1.00197	0.00094
18	0.2017	1.00059	0.00183
35	0.2096	0.99612	0.00268
40	0.2097	0.99439	0.00284
45	0.2086	0.99237	0.00304
65.3	0.1934	0.98256	0.00360
100	0.1881	—	—

The solubilities observed are lower than those found by Marignac (*Ann. Chim. Phys.*, 1874, [v], 1, 274) and by Droeze (*Ber.*, 1877, 10, 330), whilst the point of maximum solubility observed is  $40^\circ$ , instead

of  $38^{\circ}$  as found by these observers. Similarly, the values of  $\lambda$  are lower than those obtained by Kohlrausch and Rose (Abstr., 1894, ii, 7), these differences being due to the elimination of supersaturation in the present work.

T. A. H.

**Behaviour of Magnesium Chloride in a Steam Boiler.** By HERMANN OST (*Chem. Zeit.*, 1902, 26, 819—822).—The action of water on iron in the presence of air at  $100^{\circ}$  is assisted by the presence of chlorides; magnesium chloride, however, does not behave differently from other chlorides. In the absence of air, magnesium chloride corrodes iron far more readily than other chlorides. It is shown that this action is not due to the formation of hydrochloric acid, as has been supposed by Wagner; for the presence of hydrochloric acid cannot be demonstrated in tin, copper, or iron boilers at high pressures or temperatures. The author experimented with a small iron boiler, using a pressure of 10 atmospheres and a temperature of  $183^{\circ}$ ; with 5 per cent. solutions of magnesium chloride, potassium chloride, sodium sulphate, potassium sulphate, calcium chloride, and magnesium sulphate, the iron was attacked in each case, in the absence of air, even at  $100^{\circ}$ , and covered by a black layer of magnetic oxide; only in the case of magnesium salts did iron pass into solution. The oxidation and dissolution of the iron are not proportional; the former is the greater when calcium chloride, potassium chloride, potassium sulphate, or sodium sulphate is used. Since the action of magnesium chloride is not due to the formation of hydrochloric acid, neutral magnesium salts must interact with ferrous oxide. When a mixture of ferric hydroxide and iron powder, which immediately react to form the magnetic oxide, is treated with a solution of magnesium chloride at  $100^{\circ}$ , iron passes into solution as chloride; conversely, a solution of ferrous sulphate reacts with magnesium powder, forming ferrous hydroxide and magnesium sulphate. The reversible reaction is expressed by the equation:  $\text{MgCl}_2 + \text{Fe}(\text{OH})_2 \rightleftharpoons \text{FeCl}_2 + \text{Mg}(\text{OH})_2$ .

Several different kinds of iron were tested by heating with salt solutions at  $100^{\circ}$ ; in the case of all the salts just mentioned, and also with alum, the iron is attacked in the absence of air and hydrogen evolved; with alum and magnesium salts, the iron passes into solution. If hard, instead of distilled, water is used, the iron is attacked to a much less extent.

When solutions of magnesium salts are heated with calcium carbonate under a pressure of 10 atmospheres, basic magnesium carbonate, magnesium oxide, and calcium salts are formed (compare Röhrig and Treumann, *Zeit. öffentl. Chem.*, 1900, 6, 241); even in the presence of large excess of calcium carbonate, the decomposition is not complete. Since calcium salts do not cause the dissolution of the iron, the presence of calcium carbonate stops the injurious action of magnesium salts; it is found that at a pressure of 10 atmospheres it is only necessary to have present a quantity of calcium carbonate sufficient to decompose a fourth of the magnesium salts in order to prevent entirely the dissolution of iron. Under a pressure of 5 atmospheres, no action takes place with the proportion of  $2\frac{1}{2}$  parts of magnesium chloride to 1 part of calcium carbonate.

K. J. P. O.

**Cadmium Suboxides.** By SIMEON M. TANATAR and M. LEVIN (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 495—501. Compare Abstr., 1901, ii, 553).—The authors have prepared two suboxides of cadmium from the masses obtained when mixtures of cadmium oxalate and oxide are heated together. When molecular proportions of the two are heated in a glass tube, carbon mono- and di-oxides are evolved, and a dark green powder of the composition  $Cd_3O_2$  are obtained:  $3(CdC_2O_4 + CdO) = 2Cd_3O_2 + 5CO_2 + CO$ . This suboxide is decomposed by dilute hydrochloric acid with formation of cadmium chloride and very finely divided metallic cadmium. When heated, in absence of air, above its temperature of formation, the oxide is decomposed into cadmium and cadmium oxide. That this compound is not merely a mixture of cadmium and the oxide is shown by its colour, by the thermochemical data, and by the observation that it is not attacked by mercury. In presence of water, this suboxide is gradually decomposed into the hydroxide and metallic cadmium.

When the mixture heated is composed of one mol. of the oxide to two of cadmium oxalate, the reaction taking place is as follows:  $4CdC_2O_4 + 2CdO = 3Cd_2O + 7CO_2 + CO$ . This oxide, which in colour closely resembles the compound  $Cd_3O_2$ , is decomposed by dilute hydrochloric acid according to the equation:  $Cd_2O + 2HCl = CdCl_2 + H_2O + Cd$ . In presence of water, or when heated in absence of air, this oxide yields cadmium and cadmium oxide. Mercury is incapable of removing cadmium from this compound.

T. H. P.

**Thallic Chloride.** By RICHARD JOS. MEYER (*Zeit. anorg. Chem.*, 1902, **32**, 72—77).—In reply to Cushman's criticism (this vol., ii, 322) of the author's former paper (Abstr., 1900, ii, 655), it is pointed out that under certain conditions the chlorine of thallic chloride is not completely precipitated by silver nitrate. The reason for this is that silver chloride is soluble in a solution of thallic nitrate; the solubility probably depends on the formation of a double salt of silver chloride and thallic nitrate.

In spite of the fact that Cushman could not obtain it, the formation and existence of the compound with ether,  $TiCl_3 \cdot Et_2O$ , is quite certain. The best method for preparing it is to pour ether over hydrated thallic chloride,  $TiCl_3 \cdot 4H_2O$ , then separate the two layers and cool the ethereal solution in a freezing mixture, when the dissolved tetrahydrate crystallises. The ethereal solution is then placed in a desiccator over sulphuric acid, and the ether evaporated under diminished pressure. The ether compound separates in crystals. In a vacuum, it loses ether and leaves anhydrous thallic chloride. By the action of light, the ether compound is reduced, and thaloso-thallic chloride is produced. The ether compound melts below  $30^\circ$ , whilst the tetrahydrate melts at  $43^\circ$ .

The author raises objection to the structural formulæ proposed by Cushman for thallic chloride tetrahydrate and its double salts.

J. McC.

**Behaviour of Salt Solutions towards Copper and towards Iron in the Presence of Copper.** By HERMANN OST (*Chem. Zeit.*, 1902, **26**, 845—847. Compare preceding page).—When heated in



a copper boiler under a pressure of 10 atmospheres, a 5 per cent. solution of magnesium chloride dissolves copper. Similar experiments with sodium chloride and sulphate show that the copper is dissolved only in the former case; the solution of copper is colourless, and on standing deposits a pale green precipitate.

The majority of metallic chlorides are able, at  $100^{\circ}$ , to dissolve copper as cuprous chloride from cuprous oxide, or from a mixture of copper and cupric oxide. Sulphates have no such power. Pure cupric oxide is not dissolved; further, copper free from oxide is not attacked. The interior of the copper boiler could not be freed from oxide.

When iron is put in the copper boiler, dissolution of the copper does not occur; the iron becomes covered with a layer of magnetic oxide, and hydrogen is evolved; in the presence of magnesium salts, iron is dissolved. The author suggests that the corrosive action of seawater on copper pipes might be lessened if iron were present in the copper.

K. J. P. O.

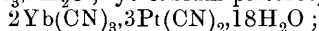
**Chemistry of Monazite Sand.** By G. PAUL DROSSBACH (*Ber.*, 1902, 35, 2826—2831).—Erbium can be separated from a mixture of basic nitrates (rich in erbium) by extraction with a solution of ammonium chloride, or with a small quantity of hydrochloric acid, thus eliminating a mixture of colourless compounds, principally of yttrium.

"Didymium" carbonate is best separated by precipitating (with a dilute solution of an alkali carbonate) its solution in a saturated solution of potassium carbonate, the precipitate thus obtained, when converted into chloride, giving the neodymium spectrum and also that of erbium and samarium. The separation of this mixture by the fractional crystallisation of the double nitrates of magnesium and the earths in question is described in detail.

The paper concludes with a discussion of various methods of separating cerium from lanthanum and didymium.

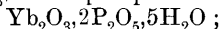
R. H. P.

**Ytterbium.** By ASTRID CLEVE (*Zeit. anorg. Chem.*, 1902, 32, 129—163).—Ytterbium has been extracted from various minerals, and after careful purification the atomic weight, determined by conversion of the oxide into sulphate, is 173.11 (three determinations). Ytterbium forms only one oxide,  $\text{Yb}_2\text{O}_3$ , which is colourless and not radioactive. The following ytterbium salts have been prepared. Ytterbium chloride,  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ , which is easily soluble in water, forms clear crystals, and decomposes at  $100^{\circ}$ ; the oxychloride,  $\text{YbOCl}$ , has not been obtained quite pure; the bromide,  $\text{YbBr}_3 \cdot 8\text{H}_2\text{O}$ ; the iodate,  $\text{Yb}(\text{IO}_3)_3 \cdot 6\text{H}_2\text{O}$ ; the periodate,  $\text{YbIO}_5 \cdot 2\text{H}_2\text{O}$ ; two double salts of ytterbium chloride with platonic chloride,  $2\text{YbCl}_3 \cdot \text{PtCl}_4 \cdot 22\text{H}_2\text{O}$  and  $2\text{YbCl}_3 \cdot \text{PtCl}_4 \cdot 35\text{H}_2\text{O}$ ; ytterbium hydrogen platinitbromide,  $\text{YbBr}_3 \cdot 3\text{H}_2\text{PtBr}_6 \cdot 30\text{H}_2\text{O}$ ; no normal double bromide could be obtained; ytterbium aurichloride,  $\text{YbCl}_3 \cdot \text{AuCl}_3 \cdot 9\text{H}_2\text{O}$ ; ytterbium platincyanide,



potassium ytterbium ferrocyanide,  $\text{K}_2\text{YbFe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ ; two nitrates,  $\text{Yb}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$  and  $\text{Yb}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ , the former by slow crystallisation from a neutral solution, the latter from a nitric acid solution; the sulphate,  $\text{Yb}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ , the solubility of which

diminishes as the temperature rises, 100 parts of water dissolve 44.2 parts of anhydrous sulphate at 0°, 11.5 parts at 55°, and 4.67 parts at 100°; the sulphite,  $\text{Yb}_2(\text{SO}_3)_3 \cdot 9\text{H}_2\text{O}$ ; the ethylsulphate,  $\text{Yb}(\text{EtSO}_4)_3 \cdot 9\text{H}_2\text{O}$ , which begins to decompose at 70°; two selenates,  $\text{Yb}_2(\text{SeO}_4)_3 \cdot 15\text{H}_2\text{O}$  and  $\text{Yb}_3(\text{SeO}_4)_3 \cdot 8\text{H}_2\text{O}$ , both of which give anhydrous selenate when heated at 110–120°; the carbonate,  $\text{Yb}_2(\text{CO}_3)_3 \cdot 4\text{H}_2\text{O}$ , and a basic carbonate,  $\text{OH} \cdot \text{YbCO}_3 \cdot \text{H}_2\text{O}$ ; the orthophosphate,  $\text{YbPO}_4 \cdot 4.5\text{H}_2\text{O}$ , the metaphosphate,  $\text{Yb}(\text{PO}_3)_3$ , and a phosphate of the formula



two vanadates,  $3\text{Yb}_2\text{O}_3 \cdot 5\text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  and  $\text{Yb}_2\text{O}_3 \cdot 15\text{V}_2\text{O}_5$ ; a basic potassium ytterbium chromate,  $\text{K}_2\text{Yb}_2(\text{CrO}_4)_2 \cdot \text{Yb}(\text{OH})_3 \cdot 15.5\text{H}_2\text{O}$ ; two molybdates,  $\text{Yb}_2\text{O}_3 \cdot 7\text{MoO}_3 \cdot 6\text{H}_2\text{O}$  and  $2\text{Yb}_2\text{O}_3 \cdot \text{MoO}_3$ ; the metatungstate,  $\text{Yb}_2\text{O}_3 \cdot 12\text{WO}_3 \cdot 35\text{H}_2\text{O}$ ; the oxytungstate,  $(\text{YbO})_2\text{WO}_4$ , which is interesting as being the first instance of the formation of a univalent positive radicle amongst the rare earths; two sodium ytterbium tungstates,  $2\text{Yb}_2\text{O}_3 \cdot 4\text{Na}_2\text{O} \cdot 7\text{WO}_3$  and  $\text{Yb}_2\text{O}_3 \cdot 9\text{Na}_2\text{O} \cdot 12\text{WO}_3$ ; the formate,  $\text{Yb}(\text{HCO}_2)_3 \cdot 2\text{H}_2\text{O}$ ; the acetate,  $\text{Yb}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot 4\text{H}_2\text{O}$ ; the propionate crystallises either with  $3\text{H}_2\text{O}$  or  $\text{H}_2\text{O}$ ; ytterbium hydrogen malonate,  $\text{YbH}(\text{C}_3\text{H}_3\text{O}_4)_2$ ; the succinate,  $\text{Yb}_2(\text{C}_4\text{H}_4\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$ ; the lactate,  $\text{Yb}(\text{C}_3\text{H}_5\text{O}_3)_3 \cdot 2\text{H}_2\text{O}$ ; ytterbium hydrogen tartrate,  $\text{YbH}(\text{C}_4\text{H}_4\text{O}_6)$ , crystallises with  $2\text{H}_2\text{O}$  or  $12\text{H}_2\text{O}$ ; ytterbium hydrogen citrate,  $\text{Yb}_2\text{H}_3(\text{C}_6\text{H}_5\text{O}_7)_3 \cdot 12\text{H}_2\text{O}$  or with  $15\text{H}_2\text{O}$ ; the benzoate,  $\text{Yb}(\text{C}_7\text{H}_5\text{O}_2)_3$ ; and the picrate,  $\text{Yb}[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}]_3 \cdot 8\text{H}_2\text{O}$ .

The conductivities of solutions of ytterbium sulphate from  $v = 3.33$  to  $v = 16667$  have been measured. Ytterbium sulphate is hydrolysed to a certain extent in dilute solution.

The oxalate is about ten times as soluble in ammonium oxalate solution as yttrium oxalate. The oxalate is also appreciably soluble in sulphuric acid.

The composition of the salts obtained clearly shows the tervalency of ytterbium. The composition of its platinoeyanide shows that it is to be grouped with yttrium, erbium, and gadolinium. J. McC.

**Electrolytic Preparation of New Alloys.** By ALFRED COEHN (*Zeit. Elektrochem.*, 1902, 8, 591–593).—From solutions of magnesium and nickel sulphates, alloys of the two metals may be deposited. These may contain as much as 10 per cent. of magnesium. The deposits are more coherent than those of pure nickel obtained in similar circumstances. T. E.

**Behaviour of Chromium prepared by the "Aluminothermal Method" towards Hydrochloric Acid.** By THEODOR DÖRING (*J. pr. Chem.*, 1902, [ii], 66, 65–103. Compare Brauer, *Abstr.*, 1901, ii, 635).—The three samples of chromium employed contained respectively 97.95, 97.41, and 93.67 per cent. of metallic chromium. As commercial aluminium always contains iron, silicon, manganese, sulphur, and phosphorus, the presence of these impurities in chromium prepared by Goldschmidt's process is difficult to avoid. The chromium dissolves, with evolution of hydrogen, in moderately concentrated hydrochloric acid at the ordinary temperature, and in very dilute acid on gentle warming. The least pure chromium enters into reaction most easily. The chromous chloride formed by solution of the chromium in hydro-

chloric acid is converted, by a secondary reaction, into chromic chloride, the change being complete if the reaction is carried out at the ordinary temperature, but less than complete if at 100°. This change is ascribed to a catalytic action of silica. If air is excluded, chromous chloride is stable in neutral solution, but in hydrochloric acid solution it has a tendency to form chromic chloride; the reaction, which is accompanied by evolution of hydrogen, is extremely slow, but is markedly accelerated by addition of platinum black, finely divided gold, or silica. The formation of chromic chloride from chromous chloride in acid solution takes place according to the equation:  $2\text{CrCl}_2 + 2\text{HCl} \rightleftharpoons 2\text{CrCl}_3 + \text{H}_2$ , and is a reversible reaction.

Ostwald's periodic curve (Abstr., 1900, ii, 730; 1901, ii, 24) is probably the resultant of two curves representing the formation of chromous chloride and its conversion into chromic chloride.

G. Y.

**Oxidisability of Chromic Hydroxide.** By UBALDO ANTONY and PAOLI (*Gazzetta*, 1902, 32, i, 518—525).—If excess of alkali hydroxide be added to a solution containing a chromium and a manganese salt in the proportion Mn:8Cr (O=16), no precipitate is obtained, but the liquid is coloured emerald green and must be regarded as a colloidal solution of the hydroxides of chromium and manganese, since this behaviour is only exhibited when the salts are present in exactly the above ratio. Chromium being trivalent and having both an acid and basic function, whilst manganese is bivalent and decidedly metallic in its properties, there is no doubt that they exist in this solution in the form of a salt, an electrolyte, which must be either a manganous chromite or polychromite. When this liquid is exposed to the air, or, better, when oxygen is passed through it, it quickly turns brown but remains free from precipitate. The element undergoing the oxidation is the manganese which becomes quadrivalent; the rôles of the two elements thus become interchanged and a more or less basic chromium manganite is formed. The chromium hydroxide now begins to undergo oxidation and the amount of chromate formed in the solution increases until about 60 per cent. of the chromium has been converted. Continued action of oxygen has now no further effect on the liquid which, after a time, deposits a dark precipitate of constant composition, the proportion Mn:Cr having the value 1:3; when this compound is treated with cold dilute sulphuric acid, the chromium dissolves as sulphate whilst the manganese remains in solution as the hydrate of manganese dioxide. If now to this liquid is added an alkaline solution of chromium hydroxide, the latter undergoes immediate and complete oxidation.

The velocity with which this oxidising action proceeds was also investigated.

T. H. P.

**Ammonium Tungstates.** By THOMAS M. TAYLOR (*J. Amer. Chem. Soc.*, 1902, 24, 629—643).—Ammonium paratungstate,  $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$ , crystallises in needles with  $11\text{H}_2\text{O}$  and in plates with  $5\text{H}_2\text{O}$ . Both forms when heated begin to lose ammonia at 60°. When boiled in aqueous solution for several days, they yield the meta-

tungstate,  $(\text{NH}_4)_2\text{W}_4\text{O}_{13}\cdot 8\text{H}_2\text{O}$ , which crystallises in tetragonal octahedra and begins to lose ammonia at  $120^\circ$ . Any one of the foregoing salts when heated at  $250^\circ$  is converted into a glass-like, colloidal tungstate of the formula  $(\text{NH}_4)_2\text{W}_6\text{O}_{19}\cdot 4$  or  $6\text{H}_2\text{O}$ . The latter is miscible in all proportions with water and absorbs ammonia readily, thereby reverting to the "meta"-salt, which in its turn passes into the undecahydrated "para"-salt in an atmosphere of moist ammonia. When the latter is heated in contact with dry ammonia, it loses water and absorbs ammonia, the following salts being stable under these conditions at the temperatures mentioned:

At $100^\circ$ .....	$6(\text{NH}_4\text{OH}, 2\text{WO}_3), \text{NH}_4\cdot\text{OH}, 4\text{NH}_3$ .
Between $110^\circ$ and $120^\circ$ , and at $150^\circ$ .....	$6(\text{NH}_4\text{OH}, 2\text{WO}_3), \text{NH}_4\cdot\text{OH}, 5(\text{NH}_3)$ .
Between $130^\circ$ and $140^\circ$ .....	$6(\text{NH}_4\text{OH}, 2\text{WO}_3), \text{NH}_4\cdot\text{OH}, 6(\text{NH}_3)$ .
At $160^\circ$ .....	$6(\text{NH}_4\text{OH}, 2\text{WO}_3), 2\text{NH}_4\cdot\text{OH}, 2\text{NH}_3$ .
„ $200^\circ$ .....	$6(\text{NH}_4\text{OH}, 2\text{WO}_3), 2\text{NH}_4\cdot\text{OH}, \text{NH}_3$ .
„ $250^\circ$ .....	$4(\text{NH}_4\text{OH}, 2\text{WO}_3), 4\text{WO}_3, 4\text{NH}_3$ .

These salts are all unstable in air and in contact with water give off ammonia and revert to the stable undecahydrated "para"-salt. The para- and meta-tungstates may also be formulated in this manner, their temperatures of formation being added for comparison:

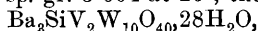
Below $100^\circ$ , "para-needles" ...	$6(\text{NH}_4\text{OH}, 2\text{WO}_3), 4\text{NH}_4\cdot\text{OH}, 6\text{H}_2\text{O}$ .
At $100^\circ$ , "para-plates" .....	$6(\text{NH}_4\text{OH}, 2\text{WO}_3), 4\text{NH}_4\cdot\text{OH}, 6\text{H}_2\text{O}$ .
„ $150^\circ$ , "meta-salt" .....	$2(\text{NH}_4\text{OH}, 2\text{WO}_3), 7\text{H}_2\text{O}$ .
„ $250^\circ$ , colloidal salt .....	$2(\text{NH}_4\text{OH}, 2\text{WO}_3), 2\text{WO}_3, 3$ or $5\text{H}_2\text{O}$ .

From this it appears that a common nucleus ( $2\text{NH}_4\text{OH}, 4\text{WO}_3$ ) runs through the whole series and that the more complex members of the group are polymerides and additive compounds derivable from this.

T. A. H.

**Silicovanadotungstates.** By CARL FRIEDHEIM and WILLIAM HOPE HENDERSON (*Ber.*, 1902, 35, 3242—3251. Compare Abstr., 1900, ii, 483).—Silicovanadotungstates can be obtained by the action of hydrofluosilicic acid on a mixture of tungstate with vanadate. From the product of reaction of ammonium vanadate on ammonium silicotungstate, an *ammonium silicovanadotungstate* of the formula  $(\text{NH}_4)_6\text{SiV}_2\text{W}_{10}\text{O}_{40}\cdot 21\text{H}_2\text{O}$  has been obtained. It forms reddish-brown, octahedral crystals of sp. gr. 3.428 at  $20^\circ$ . One c.c. of its saturated solution at  $17^\circ$  contains 0.6652 gram of the hydrated salt. If the product be not evaporated to dryness, but subjected to fractional crystallisation, a salt of the formula  $(\text{NH}_4)_6\text{SiV}_2\text{W}_9\text{O}_{37}\cdot 24\text{H}_2\text{O}$  is obtained having a sp. gr. 3.396. Two series of salts have been produced, a deca-series with the ratio of  $\text{SiO}_2$  to  $\text{WO}_3$  1 : 10, and a nono-series with the ratio 1 : 9.

The deca-salts which have been prepared are: *Sodium silicovanadotungstate*,  $\text{Na}_6\text{SiV}_2\text{W}_{10}\text{O}_{40}\cdot 29\text{H}_2\text{O}$ , in reddish-brown crystals of sp. gr. 3.344° at  $20^\circ$ ; the *potassium* salt,  $\text{K}_6\text{SiV}_2\text{W}_{10}\text{O}_{40}\cdot 22\text{H}_2\text{O}$ , in the form of reddish crystals with a sp. gr. 3.664 at  $20^\circ$ , the *barium* salt,



with a sp. gr. 3.66 at 20°. One c.c. of the saturated solution of the barium salt contains 0.0384 gram of salt. A *potassium ammonium* salt,  $\text{NH}_4\text{K}_5\text{SiV}_2\text{W}_{10}\text{O}_{40}, 23\text{H}_2\text{O}$ , soluble to such an extent that 1 c.c. of its saturated solution contains 0.5072 gram, and an *ammonium potassium barium* salt,  $(\text{NH}_4)_3\text{K}_2\text{BaSiV}_2\text{W}_{10}\text{O}_{40}, 25\text{H}_2\text{O}$ , which crystallises in holohedral forms of the regular system, have also been obtained. Potassium and barium nono-salts are obtained at the same time as the deca-salts. By the action of potassium silicotungstate on potassium vanadate, a salt of the formula  $\text{K}_{14}\text{Si}_2\text{V}_6\text{W}_{18}\text{O}_{80}, 42\text{H}_2\text{O}$  is produced, and it gives the salt  $\text{K}_{12}\text{Si}_2\text{V}_6\text{W}_{18}\text{O}_{79}, 31\text{H}_2\text{O}$  on recrystallising from water; both these are red solids which form crystals belonging to the monoclinic system. The *barium nono*-salts are:  $\text{Ba}_7\text{Si}_2\text{V}_4\text{W}_{18}\text{O}_{80}, 83\text{H}_2\text{O}$  and  $\text{Ba}_6\text{Si}_2\text{V}_4\text{W}_{18}\text{O}_{79}, 50\text{H}_2\text{O}$ ; they are both red and form rhombic crystals.

These salts are all decomposed by concentrated acids or alkalis; they give characteristically coloured precipitates with lead, silver, and mercurous salts.

J. McC.

**Pertungstic, Hyperuranic, and Pervanadic Acids.** By L. PISSARJEWSKY (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 472—483).—The author has made determinations of the distribution of hydrogen peroxide between ether and water in solutions containing tungstic acid which reacts with the peroxide forming pertungstic acid. From the results obtained, it is concluded that, in aqueous solution in presence of a large quantity of free hydrogen peroxide, pertungstic acid decomposes according to the equation:  $\text{WO}_3, 2\text{H}_2\text{O}_2 \rightleftharpoons \text{WO}_3, \text{H}_2\text{O}_2 + \text{H}_2\text{O}_2$ , whilst when less free hydrogen peroxide is present, a certain amount of further decomposition also takes place, according to the equation:  $\text{WO}_3, \text{H}_2\text{O}_2 \rightleftharpoons \text{WO}_3 + \text{H}_2\text{O}_2$ .

Similar experiments with sodium hyperuranate indicate that in aqueous solution this salt undergoes decomposition with evolution of hydrogen peroxide.

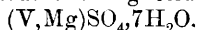
When dissolved in hydrogen peroxide, vanadium pentoxide yields pervanadic acid.

The author discusses the constitution of these hyper-acids and considers that those acids which, when acted on by sulphuric acid, give up hydrogen peroxide may be regarded as salts of the latter in which one atom of hydrogen is replaced by the radicles  $\text{VO}_2$ ,  $\text{WO}_2$ , &c. Thus, for example, pervanadic acid would be  $\text{VO}_2(\text{O}_2\text{H})$ . T. H. P.

**Some Vanadium Compounds of the Type  $\text{VX}_2$ .** By AUGUSTO PICCINI and L. MARINO (*Zeit. anorg. Chem.*, 1902, **32**, 55—71. Compare Abstr., 1899, ii, 297).—By the electrolytic reduction of vanadic anhydride in presence of sulphuric acid, *vanadous sulphate*,  $\text{VSO}_4, 7\text{H}_2\text{O}$ , is produced. This is violet and very readily oxidised. It forms monoclinic crystals which are isomorphous with  $\text{FeSO}_4, 7\text{H}_2\text{O}$ . It is very easily soluble in water. When ammonium vanadate is electrolytically reduced in presence of sulphuric acid, *vanadous ammonium sulphate*,  $\text{VSO}_4, (\text{NH}_4)_2\text{SO}_4, 6\text{H}_2\text{O}$ , is formed; it is reddish-violet and not so easily oxidised as vanadous sulphate. Its crystals are monoclinic and isomorphous with double salts of magnesium sulphate.

*Vanadous potassium sulphate*,  $\text{VSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , is formed by electrolytically reducing vanadium pentoxide along with sulphuric acid, then adding potassium sulphate, and continuing the electrolysis. It is not so highly coloured as the corresponding ammonium salt. In the same way, vanadous rubidium sulphate is formed, but it has not been possible to obtain it free from vanadium rubidium alum.

Mixed crystals of vanadous and magnesium sulphates,



and of vanadous and ferrous sulphates,  $(\text{V}, \text{Fe})\text{SO}_4 \cdot 7\text{H}_2\text{O}$ , have been formed in various proportions and it has also been shown that vanadous sulphate forms mixed crystals with chromic and other sulphates. The isodimorphism is thus proved.

If vanadic chloride solution is electrolytically reduced, using a graphite anode, the solution becomes violet, but it has not been possible to isolate vanadous chloride.

The following reactions of vanadous salts have been observed. With sodium hydroxide, a greyish-violet precipitate is obtained which quickly becomes green. Sodium carbonate gives a violet precipitate which decomposes at once. Sodium sulphide gives a violet precipitate which decomposes with evolution of hydrogen and hydrogen sulphide. With potassium nitrate and hydrochloric acid, there is an evolution of nitric oxide. From salts of tin, silver, gold, and platinum, the metal is precipitated by a solution of a vanadous salt; in the same way, copper is deposited quantitatively from its solution. It is worthy of note that chromous salts only reduce cupric salts to cuprous oxide (Peters, *Abstr.*, 1898, ii, 419). These reactions show that the vanadous compounds are to be classed amongst the most energetic inorganic reducing agents.

Attempts have been made to produce titanium compounds of the type  $\text{TiX}_3$ , but so far these have not been successful. J. McC.

**Action of Salts on Gold Chloride.** By WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1902, 316—318).—When equal volumes of dilute aqueous solutions of manganous sulphate and gold chloride are mixed and placed in the dark, metallic gold, in the form of a brown powder with a violet sheen, begins to be precipitated after from 10 to 12 days. Precipitation occurs at once if the mixture be heated to the boiling point, but sunlight exerts no accelerating influence. Uranous sulphate, under the same conditions, reduces auric chloride even more slowly; the metal is precipitated, in this case, in the form of thin films with a metallic lustre. The action is accelerated by sunlight but not by the application of heat. Manganous chloride reduces gold chloride with extreme slowness, and the mixed solutions do not deposit gold even on boiling. In sunlight, precipitation rapidly occurs. This, the author believes, is due to the influence of the radiant energy of sunlight in destroying the state of equilibrium between the reactions represented by the equation  $\text{MnCl}_2 + \text{AuCl}_3 \rightleftharpoons \text{MnCl}_4 + \text{AuCl}$ . T. A. H.

**Pulverisation and Recrystallisation of the Platinum Metals** By LUDWIG HOLBORN and F. HENNING (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 936—943).—The thermoelement platinum | platinum-irid-

ium exhibits considerable change in its *E.M.F.* after the wires have been kept at a high temperature by the passage of a current; the change in the thermoelement platinum | platinum-rhodium is very much smaller. It is now shown that when iridium and platinum-iridium alloys are kept by an electric current at a temperature near their melting point, they gradually lose in weight; the corresponding loss of weight for platinum, rhodium, and platinum-rhodium alloys is much smaller.

The authors describe how, by prolonged heating and subsequent etching, the platinum metals and their alloys, as well as gold and silver, may be obtained in a crystalline form; this part of the paper is illustrated with photographic reproductions.

J. C. P.

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## Mineralogical Chemistry.

**Dopplerite.** By HEINRICH IMMENDORFF (*Bied. Centr.*, 1902, 31, 580—582; from *Mitt. Ver. Förd. Moorkultur*, 1900, 227).—Three samples of dopplerite from (1) Oldenburg, (2) Hanover and (3) Switzerland were examined. The acidity was determined by passing hydrogen through water in which the powdered substance and calcium carbonate were suspended, both at the ordinary temperature and at 100°. The results, expressed in carbon dioxide per cent. of the dried substance, were as follows: 2.79, 1.07 and 1.52 at the ordinary temperature, and 4.43, 2.29 and 2.61 per cent. when boiled.

The dry matter of the three samples had the following percentage composition:

	Ash.	CaO.	MgO.	Fe <sub>2</sub> O <sub>3</sub> & Al <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	Insoluble in HCl.
1.	3.28	0.16	0.09	1.64	0.12	0.82
2.	2.46	0.57	0.38	1.01	0.06	0.30
3.	5.48	2.73	0.07	0.85	0.19	0.68

The organic matter of the two German samples contained carbon (1) 85.23, (2) 60.12; hydrogen, 4.77 and 5.26; nitrogen, 1.45 and 1.88; oxygen (and sulphur), 35.55 and 32.75 per cent.

N. H. J. M.

**Minerals from Casal di Pari** (in the Province of Grosseto, Italy). By G. DE ANGELIS D'OSSAT (*Atti R. Accad. Lincei*, 1902, [v], 11, i, 548—555).—There are three distinct mineral beds near Casal di Pari containing mainly antimony, lead, and mercury. In the oldest bed, known as Selva, are found stibnite (free from arsenic or lead), cervantite, stibiconite or antimonochre, sulphur, pyrites, hæmatite, gypsum and quartz. That of S. Antonio and Val d'Aspra contains galena, cinnabar, pyrites, chalcopyrite, fluorite, quartz,



limonite, azurite, malachite, calcite and gypsum. The third deposit, Miniera di Casale, is composed of quartz, pyrites, sulphur and cinnabar.

From the observations made by the author, he attributes the origin of these mineral deposits of antimony and galena to metasomatism. The cinnabar must then be regarded as a metalliferous impregnation of the quartzose vein with a formation analogous to, but not equally rich with, the cinnabar-containing quartzose veins of Almaden.

T. H. P.

**Formation of Oceanic Salt Deposits, particularly of the Stassfurt Beds. XXVII. Artificial Preparation of Pinnoite.** By JACOBUS H. VAN'T HOFF and GIUSEPPE BRUNI (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 805—807).—In beginning the study of the conditions under which boracite is naturally formed, the authors have obtained pinnoite ( $\text{MgO}, \text{B}_2\text{O}_3, 3\text{H}_2\text{O}$ ) by the dehydration in warm magnesium chloride solution of Wöhler's octohydrate,  $\text{MgO}, \text{B}_2\text{O}_3, 8\text{H}_2\text{O}$ .

J. C. P.

**Leonite from Leopoldshall.** By J. E. STRANDMARK (*Zeit. Kryst. Min.*, 1902, 36, 461—465).—Analysis of perfectly clear crystals of leonite gave results agreeing with those required for the formula  $\text{K}_2\text{SO}_4, \text{MgSO}_4, 4\text{H}_2\text{O}$ . The massive material is rendered impure by the presence of 0.5 to more than 7 per cent. of chlorine. Crystallographic measurements confirm Tenne's results (*Abstr.*, 1897, ii, 268), which, in not having been obtained from the same material as that analysed, were somewhat doubtful. Leonite is isomorphous with the artificial salt,  $\text{K}_2\text{SO}_4, \text{MnSO}_4, 4\text{H}_2\text{O}$ , but not with blödite ( $\text{Na}_2\text{SO}_4, \text{MgSO}_4, 4\text{H}_2\text{O}$ ). Twinned crystals of leonite were artificially prepared.

L. J. S.

**Dolerophanite as a Furnace Product.** By J. E. STRANDMARK (*Zeit. Kryst. Min.*, 1902, 36, 456—460).—Dolerophanite is formed in the crevices of the bed of a copper-furnace at Ätvidaberg in East Gottland, Sweden. The small, brown and brilliant crystals were found to contain:  $\text{CuO}$ , 65.95;  $\text{SO}_3$ , 34.43 per cent., corresponding with the formula  $\text{Cu}_2\text{SO}_5$ . The form of the oblique crystals also agrees with the dolerophanite formed during the Vesuvian eruption of 1868. There is a perfect cleavage parallel to {001}, and the optic axes lie in the plane of symmetry. Dolerophanite is not isomorphous with lanarkite ( $\text{Pb}_2\text{SO}_5$ ).

L. J. S.

**Alunite-Jarosite Group of Minerals.** By WILLIAM F. HILLEBRAND and SAMUEL L. PENFIELD (*Amer. J. Sci.*, 1902, [iv], 14, 211—220; and *Zeit. Kryst. Min.*, 1902, 36, 545—554).—*Natrojarosite*.—A yellowish-brown, glistening powder from the Soda Springs Valley, Nevada, consisting wholly of minute, perfectly developed rhombohedra with large basal planes, gave, on analysis, the following results (I by Hillebrand). About 6 per cent. of impurities (mainly ferric hydroxide, also  $\text{As}_2\text{O}_5$ , 0.20;  $\text{SiO}_2$ , 0.23;  $\text{CaO}$ , 0.04) were present in the material analysed. Under the microscope, the crystals are golden-yellow by transmitted light; they are optically

uniaxial and negative. Similar material, but rather more compact and schistose in character, from Cook's Peak, New Mexico, gave the partial results under II. A mineral from South Dakota, corresponding to natrojarosite, has already been described by Headden in 1893.

*Plumbojarosite*.—This material, from Cook's Peak, New Mexico, is the same in appearance and physical characters as the natrojarosite, but is darker in colour, being dark brown. It gave on analysis the results under III; the impurities present (mainly ferric hydroxide, also  $\text{SiO}_2$ , 0.51;  $\text{CuO}$ , 0.27;  $\text{CaO}$ , 0.05;  $\text{MgO}$ , 0.01) amount to 4.36 per cent.:

	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$ ?	$\text{PbO}$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{SO}_3$	$\text{H}_2\text{O}$ <105°.	$\text{H}_2\text{O}$ >105°.	Total.	Sp. gr.
I.	50.98	—	—	0.35	6.03	30.96	0.12	11.03	99.94	3.18
II.	55.60	—	0.96	0.77	4.49	—	—	—	—	—
III.	42.37	0.10	19.84	0.17	0.21	27.06	0.02	9.54	100.15	3.665

The formulæ and axial ratios of these new minerals are compared in the following table with those of the other minerals of this group. Natroalunite is the name given to the alunite from Colorado, in which  $\text{K}_2\text{O}:\text{Na}_2\text{O}=4:7$  (Abstr., 1891, 1328; 1894, ii, 458):

	Formula.	Axial ratio ( $c'$ ).
Alunite.....	$\text{K}_2[\text{Al}(\text{OH})_2]_6(\text{SO}_4)_4$	1.252
Natroalunite ...	$(\text{Na},\text{K})_2[\text{Al}(\text{OH})_2]_6(\text{SO}_4)_4$	—
Jarosite .....	$\text{K}_2[\text{Fe}(\text{OH})_2]_6(\text{SO}_4)_4$	1.245
Natrojarosite ...	$\text{Na}_2[\text{Fe}(\text{OH})_2]_6(\text{SO}_4)_4$	1.104
Plumbojarosite .	$\text{Pb}[\text{Fe}(\text{OH})_2]_6(\text{SO}_4)_4$	1.216

This series of minerals affords an illustration of the rarely occurring isomorphism between sodium, potassium and lead, but this is rather to be explained by the mass effect of the complex molecules of which these elements form a part.

L. J. S.

**Minerals from German East Africa.** By W. BORNHARDT and B. KÜHN (*Zeit. Kryst. Min.*, 1902, 36, 420—422; from *Zur Oberflächengestaltung und Geologie Deutsch-Ostafrikas. Berlin*, 1900).—In this work are given many petrographical details and descriptions of economic and other minerals. Analyses are given of the following. Epsomite, as a silky efflorescence on slate, on the Kokwamdogo stream, a tributary of the Rufiyi on the Pangani-Enge:

$\text{MgO}$ .	$\text{SO}_3$ .	$\text{H}_2\text{O}$ .	Insol. in water.	Total.
15.42	31.12	46.62	6.74	99.89

Garnet from the Namaputa stream, a tributary of the Rovuma; it has been weathered out of gneiss, in which it is embedded as rounded masses up to the size of a fist. Most pieces are of gem quality, being clear and transparent, and in colour columbine-red with a tinge of brownish-red. The following analysis shows it to be almandine rich in magnesia:

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	Total.	Sp. gr.
38.87	23.15	20.55	5.58	11.74	99.89	3.875

Titaniferous iron-ore and magnetite from the Uluguru mountains :

TiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Fe <sub>3</sub> O <sub>4</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Insol.	Total.
25.31	63.49	—	0.22	0.38	2.15	7.43	98.98
1.85	—	65.52	0.16	0.17	0.69	30.88	99.27

L. J. S.

Prehnite and other Zeolites in the Granulites of Cala Francese [in the Island of Maddalena (Sardinia)].—By CARLO RIMATORI (*Atti R. Accad. Lincei*, 1902, [v], 11, i, 542—547).—The author has made further investigations on the chabazites occurring in the granulites of Maddalena, the results obtained confirming the close analogy previously observed by him (Abstr., 1900, ii, 735) between the granulites of Maddalena and of Striegau. No fluorine has, however, been found in the former. The following five minerals from the zeolite group have been observed in the granulites of Cala Francese: stilbite, laumontite, two varieties of prehnite (one green and the other nearly white) and scolecite.

T. H. P.

Variety of Ptilolite from the Island of Principe Rodolfo. By LUIGI COLOMBA (*Atti R. Accad. Sci. Torino*, 1901—1902, 37, 553—560).—The author describes a variety of ptilolite found included in a sample of yellowish calcite from the Bay of Teplitz. The mineral occurs in long, flexible, colourless needles, which have a silky lustre, the larger ones being situated parallel to the long axis, and showing in some cases a terminal face perpendicular to the axis. Analysis gave :

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
67.52	10.76	3.31	1.69	1.19	14.43	99.90

corresponding with the formula  $(\text{Ca}, \text{K}_2, \text{Na}_2)\text{Al}_2\text{Si}_{11}\text{O}_{26} + 8\text{H}_2\text{O}$ , the relation,  $\text{Ca} : \text{K}_2 : \text{Na}_2$  having the value 3 : 1 : 1. It will be seen that this sample of ptilolite is remarkable for the large proportion of acid radicles and of water it contains. The optical properties were also studied.

T. H. P.

Mariupolite, an Extreme Member of the Elæolite Syenites. By JÓZEF MOROZEWICZ (*Tsch. Min. Mitth.*, 1902, 21, 238—246).—A complex of elæolite-syenites, varying from very coarse grained through porphyritic to compact in structure, forms, with intimately associated pyroxenites, an intrusive mass between granite and gneisses in the Mariupol district on the coast of the Sea of Azov. The following minerals were isolated from a coarse grained, porphyritic variety of the elæolite-syenites, and separately examined in detail with reference to their optical and other characters. I, Zircon (“auebachite,” compare Abstr., 1899, ii, 673); the pyramidal crystals are seen under the microscope to be much altered, but fresh portions show the ordinary optical characters of zircon; the alteration of the mineral has been accompanied by a loss of some zirconia and an introduction of water. II, Ægirite, as dark green, elongated, prismatic crystals; formula,  $9\text{Na}_2\text{Fe}_2\text{Si}_4\text{O}_{12} + \text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} + \frac{1}{3}(\text{Fe}, \text{Ca}, \text{Mg})_4\text{Si}_4\text{O}_{12}$ . III, Lepidomelane, as isolated black scales; formula,  $2\text{R}'_2\text{R}'''\text{Si}_2\text{O}_8 + \frac{1}{2}\text{R}''_2\text{Si}_2\text{O}_8$ ; the

amounts of manganese oxides and of soda are higher than is usually the case. IV, Nepheline (elæolite), as large, tabular crystals and rounded masses, which are quite fresh and transparent; the formula,  $K_2Na_8Al_{10}Si_{11}O_{42}$ , is the same as that proposed by Thugutt (Abstr., 1895, ii, 358). V, Albite, as white, finely granular, saccharoidal aggregates of prismatic crystals.

	ZrO <sub>2</sub> .	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.
I.	61·53	36·17	—	1·03	—	—	—
II.	—	51·47	2·29	30·25	1·22	0·29	0·54
III.	—	33·26	11·70	24·60*	8·51	5·04†	—
IV.	—	43·33	33·97	0·30	—	—	0·12
V.	—	67·46	19·18	0·19	—	—	0·08
VI.	1·08	62·53	18·72	3·26	0·34	0·16	0·54

	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.	Sp. gr.
I.	—	—	—	1·18	99·91	4·2
II.	0·32	trace	13·73	0·79	100·80	3·502
III.	3·00	7·78	2·46	2·50	98·85‡	3·165
IV.	—	5·40	16·07	0·96	100·15	2·625
V.	—	trace	12·07	0·64	99·62	2·622
VI.	0·08	0·79	11·77	0·68	99·95	2·699

\* Fe<sub>2</sub>O<sub>3</sub> + TiO<sub>2</sub>.† MnO + Mn<sub>2</sub>O<sub>3</sub>.

‡ F undetermined.

Under VI is given the bulk analysis of the rock, which is remarkable in showing such small amounts of bivalent metals and of potassium. In elæolite-syenites, the ratio Na<sub>2</sub>O : K<sub>2</sub>O rarely exceeds  $2\frac{1}{2}$ , but here, with an absence of potash-felspar, it reaches 24; for this albite-ægirite-syenite the name mariupolite is proposed. Besides the essential constituents mentioned above, the rock contains very small amounts of iron-ores, apatite, fluorite and sphene. The quantitative mineralogical data given below were determined by the following chemical method. By treating the powdered rock with dilute hydrochloric acid, the nepheline and lepidomelane were decomposed, and a determination of the amount of iron in the solution gave the quantity of the latter mineral; the residue of zircon, albite and ægirite, when treated with dilute hydrofluoric and sulphuric acids, left the zircon unattacked, and a determination of the amount of iron in the solution gave the quantity of ægirite.

Albite.	Nepheline.	Ægirite.	Lepidomelane (and iron-ores).	Zircon.	Total.
73·0	14·0	7·6	4·0	1·6	100·2
74·5	12·5	7·6	3·5	2·0	100·1

L. J. S.

Meteorite from Bacubirito, Mexico. By HENRY A. WARD (*Proc. Rochester (N.Y.), Acad. Sci.*, 1902, 4, 67—74).—This enormous mass of meteoric iron, although mentioned in 1876, has now for the first time been completely unearthed at Ranchito, near Bacubirito, in the State of Sinaloa. It is irregular in form, measuring about  $13 \times 6 \times 5$  feet, and is estimated to weigh 50 tons; this and the recently discovered Anighito iron of Greenland, also estimated to weigh 50 tons, are thus the largest known meteorites. The surface is covered with well-defined pits, and is only slightly weathered. The structure of the iron is octahedral to a very marked degree, and Widmanstätten figures

are shown on an etched surface in a most beautiful manner. Analysis by J. E. Whitfield gave :

Fe.	Ni.	Co.	S.	P.	Si.	Total.	Sp. gr.
88.944	6.979	0.211	0.005	0.154	trace	96.293	7.69
L. J. S.							

**Casas Grandes Meteorite.** By WIRT TASSIN (*Proc. U.S. Nat. Mus.*, 1902, 25, 69—74).—The meteoric iron described purports to be the mass mentioned in 1867 as having been found wrapped in cloth in the ancient Mexican ruins of Casas Grandes in the State of Chihuahua. It is a lenticular mass measuring  $97 \times 74 \times 46$  cm., and weighing 1,544,788 grams. Widmanstätten figures are prominent on an etched surface. A bulk analysis of the iron is given under I, but other determinations of the nickel and cobalt (Ni, 5.02; Co, 0.30; Ni, 4.50; Co, 0.00) show that the composition varies in different portions. The following minerals were isolated from the mass and analysed separately: II, troilite; III, schreibersite; IV, taenite. Graphitic carbon and an undetermined silicate are also present in small amount :

	Fe.	Ni.	Co.	Cu.	S.	C.	P.	Total.	Sp. gr.
I.	95.13	4.38	0.27	trace	—	trace	0.24	100.02	—
II.	63.40	0.20	—	—	36.21	—	—	99.81	4.789
III.	64.69	20.11	—	—	—	—	15.00	99.80	7.123
IV.	82.90	16.64	—	0.04	—	—	0.09	99.77	—
L. J. S.									

**Niagara Meteorite.** By H. L. PRESTON (*J. Geol.*, 1902, 10, 518—519).—A small mass of iron weighing 115 grams was found in 1879 near Niagara, Forks Co., North Dakota. The structure is octahedral. Analysis by J. M. Davison gave :

Fe.	Ni.	Co.	Total.	Sp. gr.
92.67	7.37	0.13	100.17	7.12

L. J. S.

**Meteorite Studies.** By OLIVER CUMMINGS FARRINGTON (*Field Columbian Museum, Geol. Ser.*, 1902, 1, 283—315).—*Long Island, Phillips Co., Kansas.*—This is the largest meteoric stone known, the total weight of the several fragments, many of which can be fitted together, being at least 564 kilos. Sp. gr. 3.45. It is traversed by planes resembling joint-planes, which are of pre-terrestrial origin; and in structure it belongs to the class of crystalline chondrites. The amount of chromite (8.83 per cent.) present is greater than in any other meteorite. The soluble silicates (24.74 per cent., mainly olivine) have the composition under I, the insoluble silicates (47.05 per cent., mainly bronzite and monoclinic pyroxenes) II, and the nickel-iron (3.31 per cent.) III. Other mineralogical constituents are: limonite (10.50), troilite (5.24), schreibersite (0.23), oxides of cobalt and nickel (0.10 per cent.).

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Cr <sub>2</sub> O <sub>3</sub> .	FeO.	CoO.	NiO.	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.
I.	36.88	6.64	1.38	18.62	—	—	0.08	36.40	—	—
II.	56.52	3.07	—	6.05	0.10	1.45	2.94	29.28	0.53	0.06

*Toluca (Los Reyes), Mexico.*—This iron weighing 19·5 kilos., said to have been found at Los Reyes, appears to belong to the Toluca fall. Analysis gave the results under IV.

*Hopewell Mounds, Ross Co., Ohio.*—A small mass of iron weighing 5 ounces was found with human remains in these Indian mounds. The distortion of the Widmanstätten figures suggests that the iron has been heated and hammered. Analysis gave the results under V.

*Tænite from the Kenton Co. Meteorite.*—The decomposition of this iron causes the separation of the mass into octahedral fragments of iron-grey kamacite, and thin elastic plates of tin-white tænite: the latter gave on analysis the results under VI, agreeing with those required for the formula  $\text{Fe}_{13}\text{Ni}_3$ .

	Fe.	Ni.	Co.	Cu.	Mn.	P.	C.	S.	Si.	Insol.	Total.
III.	78·65	20·26	1·09	—	—	—	—	—	—	—	100·00
V.	90·56	7·71	1·07	0·14	trace	0·24	0·01	0·025	0·006	0·09	99·85
V.	95·20	4·64	0·404	0·035	trace	0·07	—	0·13	(Sn, trace)		100·48
VI.	80·3	19·6		—	—	—	—	—	—	—	99·9

A description, without chemical analysis, is also given of the meteoric stone of Ness Co., Kansas.

L. J. S.

## Physiological Chemistry.

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**Air of Factories and Workshops.** By JOHN S. HALDANE (*J. Hygiene*, 1902, 2, 414—445).—A paper giving numerous results of analysis; the methods used are described in full. Among interesting points brought out are the small vitiation of the air produced when incandescent gas mantles are used, as compared with any other form of gas burner, and the advantages of the fan method of ventilation. W. D. H.

**Influence of Altitude on the Composition of the Blood.** By EMIL ABDERHALDEN (*Zeit. Biol.*, 1902, 43, 443—489. Compare this vol., ii, 619).—Numerous analytical data support the author's previous conclusion on the influence of the altitude on the composition of the blood. The principal new point brought out is an increase in the proteids of the serum with an elevated altitude. W. D. H.

**Affinity of Hæmoglobin for Carbon Monoxide and Oxygen.** By GUSTAV HUFNER (*Chem. Centr.*, 1902, ii, 459—460. From *Arch. exp. Path. Pharm.*, 48, 87—99).—At  $37.5^{\circ}$ , the relation of the reaction constant of oxygen ( $k$ ) and of carbon monoxide ( $k'$ ) towards hæmoglobin,  $x = k/k' = 0.00501$ . From this number, it is possible to estimate in any given mixture of the two gases the relative amounts of hæmoglobin with which each combines. W. D. H.

**Action of Viper Venom on the Blood of the Dog and Rabbit.** By C. PHISALIX (*Compt. rend. Soc. biol.*, 1902, **54**, 1067—1070, 1070—1071).—The action of viper venom on rabbit's blood *in vitro* is rapidly to destroy the leucocytes and promote coagulation; the red corpuscles are only slowly disintegrated, owing probably to an excess of anti-hæmolsin. The action on dog's blood is rapidly to destroy the red corpuscles, to change the hæmoglobin into methæmoglobin, and to hinder coagulation due to the liberation of anti-coagulating substances from the corpuscles. Probably here there is an excess of 'sensibiliser' which favours hæmolysis. W. D. H.

**Bactericidal Effects of Human Blood.** By A. E. WRIGHT and F. N. WINDSOR (*J. Hygiene*, 1902, **2**, 385—413).—Human serum is bactericidal to the typhoid bacillus and cholera vibrio, but has no such action towards *Staphylococcus pyogenes*, *Bacillus pestis*, or *M. melitensis*. Sterilised cultures of these organisms which are killed by the serum are distinguished from the others by directly abstracting a bactericidal element from the blood. It thus appears that the bactericidal substance must be distinct from the leucocytes which digest all bacteria. Stress is laid on the extreme risk of inoculation in man with even small amounts of the bacilli of plague and Malta fever. W. D. H.

**Disappearance of Ethers Normally Existing in the Blood.** By MAURICE DOYON and ALBERT MOREL (*Compt. rend. Soc. biol.*, 1902, **54**, 784—785). **On Lipase.** By M. DOYON and A. MOREL (*ibid.*, 785—787). By MAURICE HANRIOT (*ibid.*, 977—978). **Glycerol in the Blood.** By M. DOYON and A. MOREL (*ibid.*, 1038—1039. Compare Abstr., 1902, ii, 571).—The ethereal extract of blood diminishes if it is kept sterile at 37° without any increase in acidity, glycerol, or soaps. In the absence of oxygen, this does not occur. The next paper is polemical against Hanriot. The latter defends his position in reference to the existence of lipase. In the last paper of the series it is stated that glycerol added to the blood does not disappear, and therefore its absence after the blood has been allowed to remain at 37° is a proof that loss of its fatty matter cannot be explained by saponification.

W. D. H.

**Peptic Digestion.** By E. ZUNZ (*Beitr. chem. Physiol. Path.*, 1902, **2**, 435—480).—A large number of analytical tables are given showing quantitatively the relation between the various products of proteolysis when gastric juice is allowed to act on many varieties of pure proteid. The products are distinguished as acid albumin, primary albumoses, deutero-albumoses *A*, *B*, and *C*, true peptone, and other products which do not give the biuret reaction; the nature of these is entered into, and the proportion of aminic nitrogen determined; they are divided into two groups, those which are, and those which are not precipitable by phosphotungstic acid. The albumoses were separated by fractional precipitation with zinc sulphate. A striking feature of the tables is the frequent absence, or presence of only traces, of true peptone. W. D. H.



**Peptic Digestion of Fibrin.** By ERNST P. PICK (*Beitr. chem. Physiol. Path.*, 1902, 2, 481—513).—The products were separated by their relative solubilities in ammonium sulphate solution and in alcohol, and various albumoses are lettered and numbered. Tables showing the proportion between these and their percentage composition are given. The most notable point appears to be the disappearance of the term deutero-albumose (alluded to as “so-called”) and the appearance of two new terms, namely, *glyco-albumose* for the compound prepared from the egg-albumin rich in glucosamine, and *thio-albumose* for that from the serum-albumin rich in sulphur.

W. D. H.

**Trypsin and Erepsin.** By OTTO COHNHEIM (*Zeit. physiol. Chem.*, 1902, 36, 13—19).—Kutscher and Seemann (this vol., ii, 571) minimised the importance of erepsin in digestion. The present paper emphasises its importance.

W. D. H.

**Digestive Enzymes of some Lepidoptera.** By S. SAWAMURA (*Bull. Coll. Agric. Tokyo Imp. Univ.*, 1902, 4, 337—347).—The digestive liquids of the *Lepidoptera*, unlike those of *Vertebrata*, are all alkaline, and it is found that all the enzymes secreted in the digestive canal of silkworms cease to act in presence of acids. The proteolytic enzyme decomposes albumin into peptones; the amylolytic enzyme liquefies starch, with production of dextrin and maltose; whilst the lipatic enzyme, like that of *Vertebrata*, converts fat into fatty acids.

The three enzymes occur in the stomach, but only the proteolytic enzyme is found in the intestines.

Kruckenbergs view, that no part of the intestines of *Invertebrata* is comparable with the stomach of *Vertebrata*, is correct so far as *Lepidoptera* are concerned, since these possess no true gastric juice.

N. H. J. M.

**Rennet and Anti-rennet.** By S. KORSCHUN (*Zeit. physiol. Chem.*, 1902, 36, 141—166).—In horse serum, there is not only a specific anti-rennet, but also a pseudo-anti-rennet which inhibits rennet action, especially at 37°. It is, however, not destroyed by heat, and is easily dialysable.

W. D. H.

**The Proteolytic Action of Venins.** By L. LAUNOY (*Compt. rend.*, 1902, 135, 401—403).—The venom of the cobra, viper, and other snakes acts proteolytically, especially in an alkaline medium, on proteids (of serum and casein); this proceeds as far as the formation of proteoses, not of peptone. This power is removed by filtration through a Chamberland's bougie. The action of pancreatic juice is notably increased by the addition of snake venom (Delezenne's kinase).

W. D. H.

**Comparative Digestibility of Human Milk and its Substitutes.** By FRANCIS W. TUNNICLIFFE (*J. Hygiene*, 1902, 2, 445—451).—The experiments were carried out *in vitro*. They confirm the theory that human casein is chemically different from that of cow's milk. Using either gastric or pancreatic digestion alone, it was found that the

digestibility of the proteid matter of cow's milk and of certain patent milk foods approximates, or even exceeds, that of human casein. When, however, the total digestibility after both gastric and pancreatic digestion is considered, human milk is much more digestible than any other substitute. After 1 hour's peptic and 3 hours' pancreatic digestion, 75 per cent. of the casein is digested; the number for cow's milk is 47, and those for various patent milk foods vary from 35 to 56.

W. D. H.

**Zein as Food.** By W. SZUMOWSKI (*Zeit. physiol. Chem.*, 1902, 36, 198—218).—Dilute alkali converts zein into a modification which is soluble in water. If geese and pigeons are fed on maize, no zein is found in the organs. Introduced into the blood, zein acts as a poison (lowering of blood pressure, &c.) and is found as such in the liver. The urine contains proteid which is not zein. Immunity was not observed.

W. D. H.

**Feeding Experiments on a Dog with various Nitrogenous Materials.** By KARL KORNAUTH (*Bied. Centr.*, 1902, 31, 599—605; from *Zeit. landw. Versuchswes. Oesterr.*, 1900, 3, 1).—The various substances were made into cakes with wheat meal, and were given with small quantities of dog's biscuit alternately with meat meal, with which they were compared. Both food and excrement were analysed. "Aleuronat," which is a product of wheat starch manufacture, was found to have a high feeding value. Conglutin was inferior to both "aleuronat" and meat meal. Casein gave essentially the same results as meat meal, at any rate as regards nitrogen. Gelatin contributed relatively less nitrogen, but had a marked economising effect. Nuclein, from egg-albumin, was found to be less digestible; owing to its acidity, sugar had to be substituted for a portion of the wheat meal.

N. H. J. M.

**Behaviour of Phosphorus in Feeding.** By KARL KORNAUTH (*Bied. Centr.*, 1902, 31, 605—606; from *Zeit. landw. Versuchswes. Oesterr.*, 1900, 3, 133).—In agreement with results obtained by Bischof in 1867, it was found that when the organism is in equilibrium the faeces and urine contain the same amount of phosphorus as that of the food consumed. The author's results also confirm Marcuse's conclusion as regards the completeness of the utilisation in the intestinal canal of the phosphorus in casein, and that with a deposition of the nitrogen of casein there is coincidentally a deposition of phosphorus. In opposition to Marcuse, it was found that the phosphorus of casein is not more completely utilised than that of the other materials, even Liebermann's nuclein, but this may be due to the different experimental conditions.

N. H. J. M.

**Reactions to Stimuli in Unicellular Organisms. IX. Behaviour of fixed Infusoria.** By HERBERT S. JENNINGS (*Amer. J. Physiol.*, 1902, 8, 23—60).—The nature of the experiments is similar to those previously recorded. The fixed infusoria examined were *Stentor* and *Vorticella*. Chemical stimuli act in the main like mechanical;

to osmotic stimuli, a response is only obtained after plasmolysis is well advanced.

W. D. H.

**The Action of Inorganic Substances on Protista.** By HUGO GOLDBERGER (*Zeit. Biol.*, 1902, 43, 503—581).—The protoplasm of *Protista* behaves differently to many saline solutions than that of the higher animals, the main difference being that the osmotic pressure has little or no influence. The action is chemical, not physical. Inhibition of activity is related to morphological changes; those produced by OH or H ions are characteristic, and, death by acid or alkali, is sharply distinguished morphologically. Recovery may occur by transference to a harmless solution, but the time this takes depends on the length of previous exposure to the poison. Some reactions are not ionic, thus calcium salts are as a rule poisonous, but calcium nitrate and sulphate are harmless. Pure solutions of sodium chloride are less toxic if mixed with the chlorides of calcium and potassium.

W. D. H.

**Conservation of Muscular Energy in an Atmosphere of Carbon Dioxide.** By LHOTAK DE LHOTA (*Compt. rend.*, 1902, 135, 348—349).—In frog's muscle-nerve preparations, carbon dioxide accelerates the onset of fatigue by stopping the discharge of its energy; this is regarded as a favourable factor in preserving muscular power.

W. D. H.

**Action of Alcohol on Muscle.** By FREDERIC S. LEE and WILLIAM SALANT (*Amer. J. Physiol.*, 1902, 8, 61—74).—Pure ethyl alcohol, suitably diluted with distilled water, was injected into the dorsal lymph sac of frogs. One leg was ligatured from the effects of the drug, and used as a control for the other. In medium quantity, the effect is beneficial; the contraction is quickened, and fatigue delayed. This is due to the action of alcohol on the muscle, not on the intramuscular nerves. Beyond a certain dose, the opposite effects are obtained.

W. D. H.

**Electrical Conductivity of Animal Tissues.** By G. GALEOTTI (*Zeit. Biol.*, 1902, 43, 289—340).—The electrical conductivity of animal tissues mainly depends on the number of free ions present. On removal from the body, these probably combine with proteids, and so conductivity diminishes. Change of temperature produces a change of conductivity, increase being due to a liberation of ions from the proteid compounds. In muscle, contractibility and conductivity run parallel.

W. D. H.

**Is the Action of Ions a Function of their Electrical Charge?** By JACQUES LOEB (*Pflüger's Archiv*, 1902, 91, 248—264).—From experiments on muscle, *Medusæ*, and the skin, the conclusion is drawn that the stimulating and inhibitory effects of ions are not functions of their electrical charge.

W. D. H.

**The Time Law of the Fibrin Ferment.** By ERNST FULD (*Beitr. chem. Physiol. Path.*, 1902, 2, 514—527).—Advantage was taken of Delezenne's observations that bird's blood remains uncoagulated for

many days after removal from the body if it is not allowed to touch the muscular and other tissues, or come into contact with dirty utensils. The plasma was removed by the centrifuge, and a ferment solution prepared by making a saline extract of muscle added to it in varying quantities. Taking coagulation time, it was found that Schutz's law holds except for higher concentrations of the ferment.

W. D. H.

**Lævulose in Human Body-juices.** By CARL NEUBERG and H. STRAUSS (*Zeit. physiol. Chem.*, 1902, **36**, 227—238).—In some pathological cases, lævulose was identified in urine, serum, and ascitic, and pleural fluids. In other cases it was not found.

W. D. H.

**Comparison of the Organic Liquids of the Crab and Sacculina.** By LOUIS BRUNTZ and JEAN GAUTRELET (*Compt. rend.*, 1902, **135**, 349—350).—The saline constituents (sodium chloride and phosphates) of the secretion of the *Sacculina* and the blood of its host the crab are the same in amount. The alkalinity of the sacculina fluid is less than that of crab's blood; this is probably due to its fixation. The excreted fluid contains no free ammonia, xanthine compounds, or alkaloids; it contains lactic acid and methylamine.

W. D. H.

**Some Educts from Horse's Brain.** By ALBRECHT BETHE (*Chem. Centr.*, 1902, ii, 460—461; from *Arch. exp. Path. Pharm.*, **48**, 73—86).—By treatment of horse's brain with copper chloride, alkali, acetic acid, chloroform, and alcohol in succession, a number of substances, some in a crystalline state, were obtained; names like phrenin, aminocerebrinic acid-glucoside, &c., are given to these, some of which are stated to be identical with those previously separated out and differently named by Thudichum.

W. D. H.

**Lecithin, Kephalin, and Cerebrin from Brain.** By WALDEMAR KOCH (*Zeit. physiol. Chem.*, 1902, **36**, 134—140).—Kephalin was precipitated from an ethereal extract of sheep's brain by alcohol. Its formula is  $C_{42}H_{82}O_{13}NP$ , and it is probably dioxystearylmonomethyl lecithin. It swells and forms an emulsion with water like lecithin. The lecithin separated out yielded choline and fatty acids in such a proportion that probably there was a mixture of three possible lecithins. Cerebrin was obtained in a crystalline condition, and the analytical figures agree very well with those obtained by Thierfelder.

W. D. H.

**Composition of Human Fat.** By HERMANN JAECKLE (*Zeit. physiol. Chem.*, 1902, **36**, 53—84).—The fat of human adults consists of the glycerides of oleic, palmitic, and stearic acids. There are mere traces of lower acids. In the first months of life, there is a much higher percentage of the lower fatty acids, and much less oleic acid. No relation between the composition of the fat and the state of nutrition was observed. In fatty tumours, the amount of lecithin is considerable. In pathological conditions, it undergoes great variations, and calcium soaps are formed during conditions of calcification.

W. D. H.

**The Formation of Conjugated Glycuronic Acid in the Liver.** By GUSTAV EMBDEN (*Beitr. chem. Physiol. Path.*, 1902, 2, 591—592).—By perfusing a dog's liver with dog's blood, or a mixture of dog's and ox blood containing phenol, not only is there an increase in the combined sulphuric acid, but also of phenol-glycuronic acid. Details of the method adopted for determining these substances are given.

W. D. H.

**Thyreo-globulin.** By A. OSWALD (*Beitr. chem. Physiol. Path.*, 1902, 2, 545—556. Compare Abstr., 1901, ii, 461).—Thyreo-globulin is the main secretion of the thyroid gland and is contained in the colloidal substance. It may be combined with iodine, or not. The amount of iodo-thyreo-globulin is the main factor in the physiological activity of thyroid preparations.

W. D. H.

**Formation of Glycogen in Ascaris.** By ERNST WEINLAND and ADOLF RITTER (*Zeit. Biol.*, 1902, 43, 490—502).—Dextrose in *Ascaris* is a sure precursor of glycogen. Galactose is possibly a glycogen-sparer, but this is certainly so with levulose and maltose. Lactose has no effect, probably because *Ascaris* lacks lactase. Negative results follow the use of glycogen and other polysaccharides, whether these be injected into the animal or placed in the water surrounding it.

W. D. H.

**Composition of Milk.** By H. DROOP RICHMOND (*Analyst*, 1902, 37, 240—243).—The average monthly composition of 13,936 samples of milk analysed in 1901 is given. From his work on the proteids of milk, the author concludes that casein and albumin are not decomposition products of one proteid existing in milk. As regards the strength of casein as an acid, it was found, from the amounts of various acids required to curdle milk, that boric, acetic, and lactic acids were stronger than casein, and that the latter is an acid of the same strength as the second hydroxyl of phosphoric acid. Four analyses of human milk are also given. The sugar of human milk appears to differ from lactose, as it had, in these analyses,  $[\alpha]_D^{48.7^\circ}$  for the anhydrous sugar; the cupric reducing power was also slightly less than that of lactose.

W. P. S.

**Composition of Colostrum.** By WALTER F. SUTHERST (*Chem. News*, 1902, 86, 1—2).—Analyses of the first twenty milkings of a cow (which was milked twice a day) have been made with the following results. The sp. gr. (by pycnometer) fell rapidly from an initial value of 1.068 to 1.029 (5th milking). The total dry solids (at 105°) amounted in the first milking to 22.878 per cent., but in the second milking to 16.232 per cent., after which slight variation only was observed. The ash was 1.034 in the first and 0.874 per cent. in the second milking. The fat (by Adams' method) rose from 2.302 in the first to the normal value, 5.102 per cent., in the fifth milking. The amount of lactose was initially 2.742 per cent., and slowly increased to 4.6 per cent. at the eighth milking. At the first milking, the total proteid was 12.236 per cent., at the second 6.976, and then slowly fell to 3.464 at the seventh milking. Of the pro-

teids, casein, globulin, and albumin, the first named is initially 4.858 per cent., and then slowly decreases to the normal amount, 2.2 per cent.; globulin (estimated by precipitating with magnesium sulphate) is at the first milking 5.3206, at the second, 2.048 per cent., and then falls at first rapidly, and then more gradually, to 0.2 per cent.; the albumin shows a similar fall from 1.454 to 0.55 per cent. Equilibrium appears to be reached at the ninth milking. K. J. P. O.

[Composition of Skimmed Milk.] By FRED BORDAS and SIG. DE RACZKOWSKI (*Compt. rend.*, 1902, 135, 354—355).—The analyses given show that by skimming 98 per cent. of the cream from milk, 69 per cent. of the lecithin in the original milk was also removed.

As milk is often skimmed to the extent of 30 or even 40 per cent. of its cream, and consequently suffers a corresponding loss of lecithin, the authors state that the increasing numbers of deaths from gastrointestinal complaints are to be accounted for by this fact. It is particularly noticeable in towns where the sale of skimmed milk is permitted. W. P. S.

Human Bile. By A. TSCHERMAK (*Centr. Physiol.*, 1902, 16, 329—330).—Human bile has a slight diastatic and tryptic action. It inhibits peptic, but accelerates pancreatic, proteid digestion. Its action towards pancreatic juice is believed to be similar to that of the enterokinase of intestinal juice. W. D. H.

Effect of Injection of Micro-organisms on the Sterility of Bile. By E. SCOTT CARMICHAEL (*J. Path. Bact.*, 1902, 8, 276—279).—Injection of pathogenic bacteria into the portal circulation leaves the bile sterile; the organisms cannot pass through hepatic tissue. W. D. H.

Physiology of Leucocytes. By HENRI STASSANO and F. BILLON (*Compt. rend.*, 1902, 135, 322—325).—The elimination of various useless or poisonous materials is believed to be chiefly due to the fact that they are taken up by leucocytes, which subsequently migrate and so carry them to the exterior; this occurs through the wall of the intestine in the case of mercury, through the skin in the case of arsenic and iodine; through secreting glands, for instance, into milk in the case of several poisons. The further fact that leucocytes yield a substance which acts like Pawlow's enterokinase is also regarded as of great importance. W. D. H.

Excretion of Boric Acid in Man. By G. SONNTAG (*Chem. Centr.*, 1902, ii, 227—228; from *Arb. Kais. Ges. A.*, 19, 110—125).—Experiments on three persons who received doses of 3 grams of boric acid show that 50 per cent. of the drug is excreted in the first 12 hours; the remainder is excreted slowly, and traces are found in the urine even eight days later. Polenske's method of estimation was used. W. D. H.

The Elimination of Chlorides and Phosphates in Experimental Glycosuria. By RAPHAEL LÉPINE and MALTET (*Compt. rend. Soc. biol.*, 1902, 54, 921, 921—922).—An experiment on a dog is

recorded. Phloridzin was given, and the excretion of sugar was accompanied with a rise in the chlorides and a fall in the phosphoric acid of the urine. W. D. H.

**Glycocyamine, Glycocyamidine, and Ptomaines in Urines.** By FRANCESCO NICOLA (*Chem. Centr.*, 1902, ii, 296—297; from *Giorn. Farm. Chim.*, 51, 241—250).—Griffiths stated that the urine in cases of infectious disease, especially measles, contains ptomaines; glyco-cyamidine in particular being identified. The author has failed to confirm any of Griffiths' statements. The chemical properties of glyco-cyamine and glyco-cyamidine, which were prepared synthetically, are described. The latter is not toxic. W. D. H.

**The Oxidation Numbers of the Urine in Acid and Alkaline Solution.** By LADISLAUS NIEMIŁOWICZ and G. GITTELMACHER-WILENKO (*Zeit. physiol. Chem.*, 1902, 36, 167—197).—Fractional oxidation, with the help of indicators, especially indigo-carmin and permanganate in acid, and alizarin with potassium ferricyanide in alkaline solution, yields new methods for determining the reducing power of urine. By this means, the oxidisability of the uric acid group was estimated separately from that due to other substances, which include potassium thiocyanate. The normal values of the oxidation numbers vary in health, and are influenced by age, nutrition, and disease. W. D. H.

**Action of *Bacillus Coli Communis* on Urine.** By DIARMID NOEL PATON (*J. Path. Bact.*, 1902, 8, 280—281).—There is a form of cystitis associated with the presence of *Bacillus coli communis* in which the urine does not become ammoniacal (Melchior). Inoculation of sterile urine with the bacillus produces no change in the distribution of the nitrogen in urea, ammonia, and non-urea compounds. *B. fluorescens liquefaciens*, on the other hand, rapidly decomposes urea into ammonia, although it does not act on non-urea compounds. W. D. H.

**Conjugated Glycuronic Acids in Normal Fæces.** By MANFRED BIAL (*Beitr. chem. Physiol. Path.*, 1902, 2, 528—531). By MANFRED BIAL and O. HUBER (*ibid.*, 532—534).—Particles of fæces, and aqueous solutions of their alcoholic extract, give the orcinol reaction for glycuronic acid. Further investigation of fæces showed that conjugated glycuronic acids are really present there. On the administration of menthol with the food, the menthol compound of glycuronic acid was separated. W. D. H.

**Elimination of Carbon Dioxide in certain Metabolic Disorders.** By JOHN WALKER HALL (*J. Path. Bact.*, 1902, 8, 282—287).—Experiments on man show that pure caffeine causes increased production of carbon dioxide, but the increase varies a good deal in different people. Hypoxanthine and uric acid yield negative results; the effect of caffeine is apparently due to its methyl groups. W. D. H.

**Kinase in Snake Venom.** By C. DELEZENNE (*Compt. rend.*, 1902, 135, 328—329).—Snake venom, like leucocytic extracts, contains a substance (enzyme) which has the properties of Pawlow's enterokinase. Whether it is of use to the animal in digestion, or is the same substance as the toxin, are questions which still await an answer.

W. D. H.

**Ricin Immunity.** By MARTIN JACOBY (*Beitr. chem. Physiol. Path.*, 1902, 2, 535—544. Compare Abstr., 1901, ii, 673).—By mixing ricin with uncoagulable blood, the plasma obtained by the centrifuge contains a poison, which has no agglutinating action, but kills animals with typical symptoms. Part of the poison, however, is held back by the corpuscles. Antiricin inhibits the action of the poison in the plasma. The serum of animals immunised with the plasma poison neutralises the agglutinating and toxic action of ricin. The plasma poison requires less antiricin to neutralise it than ordinary ricin. Pepsin-ricin only agglutinates slightly, but by its use an immune serum is obtained which counteracts both properties of ricin. The blood corpuscles of a highly immunised goat were still agglutinated by ricin. Ricin probably contains three physiological groups: a toxin toxoid; an agglutinin toxoid; and the complete poison. Anti-substances are probably present in the tissue cells as well as in the blood.

W. D. H.

**Action of Erepsin and Intestinal Juice on Toxins and Abrin.** By NADINE SIEBER and C. SCHUMOFF-SIMONOWSKI (*Zeit. physiol. Chem.*, 1902, 36, 244—256).—Erepsin does not lessen the toxicity of abrin; it thus resembles other enzymes. Tetano-toxin is most strongly acted on by a mixture of trypsin and bile. Gastric juices and oxydases lessen its power somewhat, but erepsin and intestinal juice have practically no effect on it. Diphtheria toxin is energetically destroyed by the trypsin-bile mixture. Trypsin alone has considerable action; gastric juice has a smaller action, and erepsin acts like gastric juice; intestinal juice itself has only a small effect. Oxydases act more powerfully than gastric juice. Numbers illustrative of these facts are given.

W. D. H.

**Anti-paramœcic Serum.** By LEDOUX-LEBARD (*Compt. rend.*, 1902, 135, 298—299).—After five or six injections of cultures of *Paramœcium caudatum* under the skin of the rabbit or guinea-pig, the serum of these animals acquires a toxic action in relation to the organism which is greater than that possessed by it in the normal state. The substance to which this is due is not destroyed by heating at 58—63° for half-an-hour. It is a specific action; the serum kills *P. caudatum*, but not other species of *Paramœcium*.

W. D. H.

**Behaviour of Theophylline in the Dog.** By MARTIN KRÜGER and JULIUS SCHMID (*Zeit. physiol. Chem.*, 1902, 36, 1—12).—If 15.9 grams of sodium theophyllate, corresponding with 12 grams of theophylline, are given to a dog, 2.13 grams are excreted as unchanged theophylline and 1.99 grams as 3-methylxanthine, but no 1-methylxanthine is found.

W. D. H.



**Physiological Action of some Reduced Pyrrole Derivatives (Pyrroline, 1-Methylpyrrolidine).** By FRANCIS W. TUNNICLIFFE and OTTO ROSENHEIM (*Chem. Centr.*, 1902, ii, 390—391; from *Centr. Physiol.*, 16, 93—97).—The physiological action of 1-methylpyrrolidine resembles that of nicotine, and corresponds with the close relationship of its chemical constitution to that of nicotine, atropine, and cocaine.

Pyrrole and derivatives containing the pyrrole ring are characterised by their paralysing action on the peripheral nerves connected with the mechanism of the heart; by the introduction of a side group such as, for instance, the inactive pyridine ring, the pharmacological effect is greatly intensified.

The paper also contains a detailed description of the physiological action of pyrroline hydrochloride, pyrrolidine and 1-methylpyrrolidine hydrochloride and tartrate.

E. W. W.

**Pharmacodynamic Properties of certain Aromatic Semicarbazides.** By AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and J. CHEVROTTIER (*Compt. rend.*, 1902, 135, 187—188).—Phenylsemicarbazide, bromophenylsemicarbazide, methoxy-, and ethoxy-phenylsemicarbazide, and *m*-benzaminosemicarbazide are endowed with antipyretic properties. When introduced into the stomach or cellular tissue of animals, they produce a lowering of temperature without any other noticeable effects. *m*-Benzaminosemicarbazide is the most suitable of these for antipyretic purposes, on account of its stability, solubility, and ease of preparation. The toxicity of this semicarbazide has been determined, as well as its effect on the circulation, respiration, and nutrition, and its antiseptic and antifermentative actions.

J. McC.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Critical Observations on the Theory of Fermentation. (I).**  
By ANDREAS RICHTER (*Centr. Bakt. Par.*, II, 1902, 8, 787—796).—  
An examination of the ratio of carbon dioxide produced to oxygen consumed by yeast during an alcoholic fermentation of sugar in presence of peptone, shows that during the early stages this ratio is about 1, but that it then increases considerably, remains high until all the sugar has been fermented, and again falls, generally to about 0.6. It appears probable that at first the yeast cells simply grow without producing fermentation; zymase is then developed in them and fermentation proceeds to the end, after which the cells again simply make use of the nutriment still present (alcohol or peptone) for purposes of growth. The theory of Iwanowsky (*Diss.*, St. Petersburg, 1894) that alcoholic fermentation is a pathological phenomenon in the nourishment of yeast, brought about as a result of the abnormal composition of the nutrient liquid, is therefore groundless.

A. H.

**Cultivation of *Bacillus Lepræ*.** By G. VAN HOUTUM (*J. Path. Bact.* 1902, 8, 260—275).—A method of successfully cultivating the bacillus of leprosy is described. The 'sensibiliser' which attaches itself to the bacilli only occurs in leper serum. The susceptibility of the bacilli to the action of leper serum explains the numerous failures to cultivate them. W. D. H.

**Bacteriology of Soil.** By THEODOR REMY (*Centr. Bakt. Par.*, II, 1902, 8, 657—662, 699—705, 728—735, 761—769).—Four soils of different origins were carefully compared as regards (1) chemical and physical composition; (2) behaviour towards peptone solution (putrefactive power), the percentage of the total nitrogen which could be liberated by magnesia after varying times being estimated; (3) capacity for producing nitrates; (4) capacity for destroying nitrates; (5) power of utilising the nitrogen of albumin, ammonium sulphate, and sodium nitrate in the production of vegetation, and (6) total number of bacteria present at different periods of the growth of vegetation.

As a result, it was found that the putrefactive, nitrate-forming, and nitrate-destroying powers of the soil stood in a very direct relation to the power of the soil to utilise the nitrogen of different types of nitrogenous manures in the production of vegetation. The number of bacteria present, on the other hand, afforded no indication of the degree of fertility of the soil. It was also found that a soil which was of very low fertility could not be greatly improved by the simple inoculation of bacteria of the type which was lacking. A. H.

**Influence of Varying Amounts of Carbon Dioxide in the Air on the Photosynthetic Process of Leaves and on the Mode of Growth of Plants.** By HORACE T. BROWN and F. ESCOMBE (*Proc. Roy. Soc.*, 1902, 70, 397—413).—Several varieties of plants were grown in ordinary air, containing 3.29 parts of carbon dioxide per 10,000, and in air containing about three and a half times more carbon dioxide (11.47 per 10,000). The effect of the larger amount of carbon dioxide became, in most cases, apparent within a week or ten days and then rapidly increased. There was usually an increased number of internodes and, coincidentally, a shortening of the internodes, so that the height of the plants was not essentially altered. A characteristic result was the development of secondary axes in the axils of the leaves, giving the plants a more bushy appearance. The area of the individual leaves was a good deal reduced, and the leaves were frequently curled inwards, which suggests an attempt on the part of the plant to reduce the excessive absorption of carbon dioxide by diminishing the exposure to light. Under the influence of an increased supply of carbon dioxide, the leaves assumed a darker colour and accumulated much larger amounts of starch than under normal conditions. The most important result was the almost complete inhibition of inflorescence.

Of the various plants experimented on, *Impatiens platypetala* suffered most severely in the earlier stages of growth, losing nearly all its leaves. A second growth of small, very dark green leaves was, however, produced.

Further experiments with air containing 6 per cent. of carbon dioxide gave similar results. N. H. J. M.

**Influence of Carbon Dioxide in the Air on the Form and Internal Structure of Plants.** By J. BRETLAND FARMER and S. E. CHANDLER (*Proc. Roy. Soc.*, 1902, 70, 413—423).—The plants grown in ordinary air and in air containing an excess of carbon dioxide (see preceding abstract) were subjected to further examination, attention being especially directed to the relative dimensions of the internodes, the average relative areas of the leaves, the number of stomata per unit of area of leaf surface, the anatomical differences, and the relative amounts of starch, &c.

Except in the case of *Kalanchoë Welwitschii* there was always an increased accumulation of starch in the leaves and ground parenchyma under the influence of an excess of carbon dioxide. In *Kalanchoë*, the ground cells of the stomata contained more starch than when grown under normal conditions, whilst the amount of tannin was very much reduced. The plants which, under the usual conditions, contain crystals of calcium oxalate, contained less when grown in an excess of carbon dioxide except, perhaps, in the case of fuchsia.

The experiments of E. C. Téodoresco (*Rev. Gen. Bot.*, 1899, 2), which indicated greater luxuriance under the influence of excessive carbon dioxide, differed materially from those described above, none of the plants being grown in normal air, but only in air free from carbon dioxide or in presence of 1.5 to 2 per cent. The air was, moreover, partially dried by means of sulphuric acid, and this might tend to promote transpiration. N. H. J. M.

**Certain Relations of Plant Growth to Ionisation of the Soil.** By AMON B. PLOWMAN (*Amer. J. Sci.*, 1902, 14, 129—132).—A large number of pot and water-culture experiments were made, in which the plants were subjected to the action of electricity. Platinum, or, more usually, carbon electrodes were employed. In the case of the soil experiments, an excessive rise of temperature was avoided by addition of water; in the water-culture experiments, the temperature was kept down by means of cold water round the vessels.

The results indicate that vegetable protoplasm is quickly killed by the conditions existing about the anode, whilst within fairly broad limits it is stimulated by the conditions about the cathode. The effects observed cannot be attributed to the slight chemical changes due to dissociation and the electrical separation of the ions.

N. H. J. M.

**Action of Chloroform Vapour on Resting Seeds.** By B. SCHMID (*Bied. Centr.*, 1902, 31, 646; from *Ber. deut. bot. Ges.*, 1901, 19, 71).—Whilst chloroform vapour acts as a poison on the plasma, the effect on dry seeds depends on the nature of the covering of the seeds. Garden cress was not injured by being kept for two months in air saturated with chloroform vapour, whilst a small portion of the peas and wheat was destroyed in 24 hours. All the seeds, when deprived of their skins, were destroyed in 24 hours. N. H. J. M.

**Protein Grains in Oleaginous Seeds.** By BILLE GRAM (*Landw. Versuchs-Stat.*, 1902, 57, 257—296).—The skins of protein grains were generally found to resist the action of moderately strong aqueous potash. In some cases, when the potash causes the skins to burst, sections boiled in alcohol may be employed. The grains contain a substance soluble in water and in alcohol, and having the properties of cane sugar. *Ricinus* globoids were found to contain succinic acid in addition to the substances detected by Pfeiffer. The globoids of the other seeds examined seem to have the same chemical composition.

The globoids of fennel contain magnesium and calcium phosphate, malate, and succinate, and this probably holds good generally in the case of the proteids of umbelliferous plants.

Crystalloids may occur as crystals or in rounded off forms in single seeds, and they may be accompanied by proteid grains free from crystalloids. N. H. J. M.

**Ammonium as Direct Source of Nitrogen for Plants.** By P. KOSOWITSCH (*J. exper. Landw.*, 1901, 635—636).—The plan of the experiments was to grow peas, manured respectively with ammonium sulphate and sodium nitrate, under conditions of sterilisation.

At the conclusion of the experiment, it was found that the sterilisation had not been completely maintained; both the plants and the nutritive solutions were, however, free from nitrates. The results showed that when manured with ammonium sulphate the peas grew as well as in presence of nitrate. The plants developed especially well when ferric hydroxide was substituted for calcium carbonate (compare Maze, *Ann. Inst. Pasteur*, 1900, 26). N. H. J. M.

**Formation of Asparagine in the Metabolism of Shoots.** By U. SUZUKI (*Bull. Coll. Agric. Tokyo Imp. Univ.*, 1902, 4, 351—356).—The results of experiments with barley and dry beans showed that whilst in cultivated shoots decomposition of protein takes place in absence as well as in presence of oxygen, there was an increase of asparagine only when oxygen was present. Primary amino-compounds decrease with the production of asparagine. N. H. J. M.

**Amount of Lime Contained in Phanerogamic Parasites.** By K. ASŌ (*Bull. Coll. Agric. Tokyo Imp. Univ.*, 1902, 4, 287—289).—The ash of *Cuscuta europæa* contains only about 2 per cent. of lime, whilst clover, its host, yields an ash with more than 30 per cent. This, together with Palladius's observation that etiolated leaves of *Vicia faba* contained less lime than green leaves and the fact that seedlings generally require less lime before than after they have chlorophyll, accords with the inference that, not only the nuclei, but also the chlorophyll bodies require lime. In this connection, another non-chlorophyllous plant, *Gastrodia elata*, was investigated.

The dry matter of (1) the above ground and (2) the underground parts contained respectively 5.25 and 3.04 per cent. of ash of the following composition:

	K <sub>2</sub> O.	Na <sub>2</sub> O.	CaO.	MgO.	Fe <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	SiO <sub>2</sub> , &c.
1.	44.25	7.22	7.31	6.99	1.81	28.57	3.73	0.12
2.	50.99	13.73	5.08	6.37	2.59	17.24	1.85	2.15

The ratio of lime to magnesia in the above-ground parts of *Gastrodia* is therefore 1:1 as compared with flowering cereals 2:1, and lucerne before flowering 8:1 (compare Church, Trans., 1879, 35, 33; 1880, 37, 1, and 1886, 49, 839). The results lend support to the view that the chlorophyll determines the ratio between lime and magnesia.

N. H. J. M.

**The Colouring Matter and the Sugars of Apricots.** By A. DESMOULIÈRE (*Ann. Chim. anal.*, 1902, 7, 323—324).—Apricots contain chiefly sucrose with a little invert sugar and also a small quantity of free dextrose which seems to become less when the fruit ripens.

The colouring matter is extracted by amyl alcohol from either acid or ammoniacal solution. It is distinguished from coal-tar colours by not dyeing either wool or silk, but it is coloured blue on adding sulphuric acid. Probably it is closely related to carotene. L. DE K.

**Mucilage of the Prickly Pear (*Opuntia vulgaris*).** By V. HARLAY (*J. Pharm. Chim.*, 1902, [vi], 16, 193—198).—The mucilage obtained from the cactus *Opuntia vulgaris* consists for the most part of araban and galactan; its solution is dextrorotatory (+35°), and in its behaviour it more closely resembles the gums than the pectins.

H. R. LE S.

**Amount of Oil in Cotton Seeds of Various Origins cultivated in Central Asia.** By D. TSCHERNEVSKY (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 503—504).—When grown in Central Asia, cotton seeds from America or Egypt contain from 21·19 to 23·46 per cent. of oil, whilst those from Bokhara have only 17·15—17·75 per cent.

T. H. P.

**Oil of the Red Elderberry, *Sambucus Racemosa* var. *Arborescens*.** By H. G. BYERS and PAUL HOPKINS (*J. Amer. Chem. Soc.*, 1902, 24, 771—774).—The oil, extracted from the expressed juice of the berries by ether, is of a light yellow colour, which becomes darker on exposure to light or heat. It has a sp. gr. 0·9072 at 15°, solidifies at -8° and melts at 0°. The oil contains 6·65 per cent. of free acid, calculated as oleic, and yields on hydrolysis 11·4 per cent. of glycerol, which is originally present in the form of palmitin, olein, and linolein (?), with small quantities of caprin, caproin, and caprylin. The unsaponifiable matter amounts to 0·66 per cent. The saponification number is 209·3, the iodine number 81·44, the Hehner number 91·75, and the Reichert-Meissl value 1·54.

T. A. H.

**Composition of the Nuts of *Ginkgo Biloba*.** By U. SUZUKI (*Bull. Coll. Agric. Tokyo Imp. Univ.*, 1902, 4, 357—358).—The dry matter of the nuts freed from shells had the following percentage composition:

Total nitrogen.	Proteid	Crude fat.	Lecithin.	Crude fibre.	Starch.	Sucrose.	Reducing sugar.	Ash.
1·8	1·4	2·6	0·17	1·2	62·4	5·2	1·4	3·0

Cholesterol was not detected. The composition of the pure ash, including carbon dioxide, was as follows:

K <sub>2</sub> O.	Na <sub>2</sub> O.	CaO.	MgO.	Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	SO <sub>2</sub> .	SiO <sub>2</sub> .	Cl, &c.
47.3	6.0	2.7	6.3	1.7	26.4	6.0	0.5	trace

N. H. J. M.

**Indian Ipecacuanha.** By BENJAMIN H. PAUL and ALFRED J. COWNLEY (*Pharm. J.*, 1902, [iv], 15, 256—257).—A sample of Indian ipecacuanha was found to contain emetine 1.39, cephaeline 0.50, and psychotrine 0.09 per cent.

E. G.

**Chemistry of Solanum Dulcamara.** By FREDERICK DAVIS (*Pharm. J.*, 1902, [iv], 15, 160—161).—An examination of *Solanum dulcamara* has revealed the presence of solanine, solanidine, solanein, and dulcamarin. The ripe fruit also contains 0.3—0.7 per cent. of malic acid. Solanine (m. p. 235°), solanidine (m. p. 205°), and solanein are represented by the formulæ C<sub>42</sub>H<sub>75</sub>O<sub>12</sub>N, C<sub>41</sub>H<sub>71</sub>O<sub>2</sub>N and C<sub>48</sub>H<sub>78</sub>O<sub>13</sub>N respectively.

E. G.

**Variation in the Occurrence of Salicin and Salinigrin in different Willow and Poplar Barks.** By HOOPER A. D. JOWETT and CHARLES E. POTTER (*Pharm. J.*, 1902, [iv], 15, 157—159).—In order to determine the species of *Salix* which yields salinigrin (Jowett, *Trans.*, 1900, 77, 707), a large number of species of *Salix* and *Populus* have been examined. Salinigrin was found in one case only, *Salix discolor*, whilst salicin was detected in eight species, but in only two of these was it present in sufficient quantity to be isolated. It was found that the amount of salicin contained in the bark of a willow or poplar depends, not only on the species, but also on the season of the year in which it is collected, the sex of the tree, and possibly other factors.

E. G.

**Decomposition of Fodder and Food by Micro-organisms.**  
**II. Organisms Destroying Bread.** By JOSEF KONIG, ALB. SPIECKER-MANN, and J. TILLMANS (*Zeit. Nahr. Genussm.*, 1902, 5, 737—763. Compare Abstr., 1901, ii, 676).—The action on bread of *Bacillus viscosus* I and II and *B. panis viscosus* I Vogel was accompanied by decomposition of carbohydrates and nitrogenous substances, starch being dextrinised. The fat and crude fibre appeared to be little attacked. As the result of the decomposition of the proteids, free ammonia was formed, and the amount of soluble nitrogenous compounds increased. The acidity of the attacked bread also increased, as compared with the original bread. Experiments on starch showed that the bacteria partially converted it into dextrin and sugars. With yeast, the same alterations were noticed as in the case of bread. An investigation was also carried out on the chemical nature of the “ropiness” of the bread which was produced by the bacteria. Estimations were made of the nitrogen, water, ash, pentosans, and other carbohydrates, after separating the substances into two portions, one soluble and the other insoluble in 50 per cent. alcohol. The former contained:

water, 10.30; nitrogen, 1.61; carbohydrates (after 6 hours' inversion with hydrochloric acid), 42.50; pentosans, 3.48; and ash, 5.48 per cent. The insoluble portion contained: water, 4.49; nitrogen, 8.80; carbohydrates (inverted), 16.74; pentosans, 3.83; and ash, 7.78 per cent.

W. P. S.

**Sunflower Cake.** By RICHARD WINDISCH (*Landw. Versuchs-Stat.*, 1902, 57, 305—316. Compare Abstr., 1894, ii, 155).—The materials examined were all of Hungarian origin. The average composition was found to be as follows:

	Water.	Crude protein.	Crude fat.	N-free extract.	Crude fibre.	Crude ash.
Sunflower seeds ...	6.88	15.19	28.79	17.36	28.54	3.20
„ kernels..	4.00	24.93	50.44	12.83	3.14	4.01
„ husks ...	10.09	6.91	7.87	20.84	51.57	2.69
„ cake ...	5.11	35.62	16.77	24.08	11.69	6.84

N. H. J. M.

**Mill Refuse of Rye and Wheat.** By FRITZ OTTO (*Bied. Centr.*, 1900, 31, 606—610; from *Inaug. Diss. Göttingen*, 1901).—Analyses of the various products from rye and wheat. Determinations of digestibility were also made.

N. H. J. M.

**Amounts of Potassium and Phosphoric Acid in the Ashes of Leaves of Varieties of Potatoes Rich in Starch.** By JOSEF SEISSL and EMANUEL GROSS (*Chem. Centr.*, 1902, ii, 383—384; from *Zeit. Landw. Versuchswes. Oesterr.*, 5, 862—875).—Potassium applied as kainite increased both the yield of tubers and the amount of starch. Superphosphate alone was injurious, both as regards quantity and yield. When both manures were applied, the injurious effect of superphosphate was diminished but not overcome. In every case there was increased leaf production; the leaves were light coloured and yellowish when phosphoric acid was applied (even when in conjunction with potash), but normal with kainite alone.

The ash of leaves of potatoes rich in starch contained more potassium and phosphoric acid than in the case of potatoes poor in starch. The difference was observed all through the vegetative period, and with different manures. As regards the action of manures on the composition of the leaf ash, only phosphoric acid, and, in some cases, potassium, had any effect.

N. H. J. M.

**Manurial Experiments with Forty per cent. Potassium Salts on Potatoes on Peat Soil.** By BRUNO TACKE (*Bied. Centr.*, 1902, 31, 584—585; from *Flugblatt. Bremen*, Dec., 1900).—Forty per cent. “potassium manure salts” gave better results with potatoes than kainite. In the case of newly cultivated peaty soil, 175 to 150 kilos. of potash may be applied, whilst an application of about 100 kilos. per hectare will suffice for similar soil which has been longer cultivated. The best time for applying the salts for potatoes is towards the end of winter.

N. H. J. M.

**Constituents of Emmenthaler Cheese.** By ERNST WINTERSTEIN and J. THÖNY (*Zeit. physiol. Chem.*, 1902, 36, 28—38. Compare Weidmann, *Land. Jahreshbucher*, 1882, 587).—During the process of



ripening of Emmenthaler cheese, the fatty constituents undergo but little change; the chief nitrogenous constituent, paracasein, on the other hand, undergoes complex decompositions resulting in the formation of ammonia, amino-acids, and proteid substances soluble in alcohol (caseoglutin). The chief basic constituents which have so far been identified are histidine, lysine, pentamethylenediamine, tetramethylenediamine, and probably guanidine.

Arginine has not been detected; it is presumably formed, but during the ripening process undergoes decomposition, probably into guanidine and tetramethylenediamine.

In only one cheese, a very old one, has any appreciable amount of tyrosine been found, and then it has a very low dextrorotation.

J. J. S.

**Chemical Methods for Estimating the Fertility of Soils as regards Phosphoric Acid.** By K. K. GEDROIZ (*Jour. exper. Landw.*, 1901, 768—769).—Determinations of the phosphoric acid in soils were made by Maercker's method (action of 300 c.c. of 2 per cent. citric acid on 60 grams of soil for 24 hours), and by Bogdanoff's method (digesting 1 kilo. of soil for 24 hours with 4 litres of 2 per cent. acetic acid). At the same time, pot experiments were made in which various plants were grown in the same soils. The results showed that the different plants took up unequal amounts of phosphoric acid, and that barley and flax assimilated amounts differing considerably from those dissolved by 2 per cent. acetic acid. On the whole, citric acid gave better results than acetic acid. N. H. J. M.

**Solution of Phosphoric Acid in Soil Water.** By G. PATUREL (*Ann. Agron.*, 1902, 23, 385—398).—The total phosphoric acid and the phosphoric acid soluble in water (by extracting 300 grams of soil with 1300 c.c. of water) both before and after addition of superphosphate (0.1 per cent.) was determined in six soils: (1) calcareous clay (from lias), (2) sandy clay, (3) sandy soil (derived from granite), (4) slightly calcareous sand, (5) humous sand, and (6) garden soil. The following results were obtained:

	CaCO <sub>3</sub> , per cent.	P <sub>2</sub> O <sub>5</sub> , per cent.	P <sub>2</sub> O <sub>5</sub> soluble in water (mg. per litre).	
			Unmanured.	With superphosphate.
1.....	12.8	0.717	0.42	2.60
2.....	0.4	0.183	0.09	0.55
3.....	0.5	0.119	0.86	15.03
4.....	3.5	0.171	1.55	4.45
5.....	0.4	0.246	1.84	8.31
6.....	9.6	0.409	2.93	—

The results show that there is no relation between the total and soluble phosphoric acid, and that the proportion of the phosphoric acid applied which is retained by the soil has no connection with the amount of calcium carbonate present. The results obtained with soil (5) are of interest, as this is a typical hemp soil, and hemp has a very short vegetative period and requires plenty of available food. The soil

(3), which gave the highest result, is a vine soil which for years had given very good results when manured with superphosphate. Further experiments were made with the samples of this soil obtained five months after the application of superphosphate. Although there had been much rain since the manure was applied, the aqueous extract obtained after five months contained nearly 10 milligrams of phosphoric acid per litre.  
N. H. J. M.

**Action of Potassium Manures on Peat Land.** By ANTON BAUMANN (*Bied. Centr.*, 1902, 31, 585—589; from *Vierteljahrsschr. Bayer. Landw.*, 1901, Heft. 1; and *Arb. deut. landw. Ges.*, Heft. 56).—Potassium carbonate and sulphate are the best potassium manures for potatoes on peat soil, and potassium chloride ( $K_2O = 40-50$  per cent.) is a much better manure than salts containing a low percentage of chlorine, especially kainite. Eight years' manuring with salts containing a high percentage of potassium, without lime or marl, was without injurious effect.  
N. H. J. M.

**Influence of different Ratios of Lime and Magnesia on the Development of Plants.** By K. Asō (*Bull. Coll. Agric. Tokyo Imp. Univ.*, 1902, 4, 361—370).—Soy beans require a greater excess of lime over magnesia than is the case with wheat, barley, and onions. The difference is attributed to the greater leaf surface produced in a given time by the beans.

The proper ratio between lime and magnesia is of great practical importance and in liming a soil not only the amount of lime already present, but especially its relation to the magnesia, should be considered. The poisonous effect of magnesia in absence of lime and the influence of the latter on the production of root hairs, already observed by Loew, were confirmed.  
N. H. J. M.

**To what extent should a Soil be Limed?** By T. FURATA (*Bull. Coll. Agric. Tokyo Imp. Univ.*, 1902, 4, 371—379).—The most favourable ratios  $CaO/MgO$  for buckwheat, cabbage, and oats were found to be 3:1, 2:1, and 1:1 respectively. Before liming a soil, the readily available lime and magnesia should be determined, after which lime should be added in such quantity as will give the desired ratio, according to the kind of crop to be grown.  
N. H. J. M.

**Lime Factor for different Crops.** By OSCAR LOEW (*Bull. Coll. Agric. Tokyo Imp. Univ.*, 1902, 4, 381—385. Compare preceding abstracts and Loew and May, this vol., ii, 622).—In reference to the importance of lime to cereals, especially before the flowering period, it is suggested that the application of a very dilute solution of calcium nitrate to the young plants might be very beneficial.

The injurious effects of an excess of magnesia (even a 0.1 per cent. solution of magnesium nitrate) on nuclei and chlorophyll bodies can be seen with a microscope in the case of filaments of *Spirogyra*.  
N. H. J. M.

**Relative Power of Agricultural Plants to Utilise the Phosphoric Acid of Crude Phosphates.** By P. KOSSOWITCH (*J. exper. Landw.*, 1901, 730—733).—Mustard and buck wheat grown

in pots gave as good yields with phosphorite as with basic slag, whilst clover and flax were less able to utilise the phosphoric acid of phosphorite. Winter rye gave very unsatisfactory results with phosphate as compared with basic slag.

N. H. J. M.

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## Analytical Chemistry.

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Filter-paper; a Source of Error in Chemical Analysis. (i) Retention of a Dissolved Substance by Filter-paper and by Cotton; (ii) Unequal Spreading of a Substance in Solution when placed on Filter-paper. By MANSIER (*J. Pharm. Chim.*, 1902, [vi], 16, 60—64; 116—120).—When solutions of solid substances are filtered through filter-paper or cotton, the filtered solution generally contains less of the dissolved substance than it did before filtration, owing to the fact that the filter-paper or cotton absorbs an appreciable amount of the dissolved substance. This is particularly the case with solutions of the alkalis, sulphuric acid, and the salts of the alkaloids. Sodium chloride and certain other salts, however, are not thus absorbed.

When a drop of the solution of a solid substance is placed on filter-paper, the outer zone of the moistened portion is very often entirely free from the dissolved substance. These facts may, in the author's opinion, lead to serious errors in chemical analysis. H. R. LE S.

Titration with Phenolphthalein in Alcoholic Solution. By ROBERT HIRSCH (*Ber.*, 1902, 35, 2874—2877).—One hundred c.c. of neutral 96 per cent. alcohol, containing 5 mg. of phenolphthalein, is coloured only a pale rose by 0.1 c.c. of *N* sodium hydroxide, whereas in aqueous solution an intense colour is developed. On heating the aqueous solution, the colour fades, but that of the alcoholic solution becomes much deeper. In methyl alcoholic solution under similar conditions, no colour appears. Warm solutions of normal sodium acetate and stearate in alcohol give a strong coloration with phenolphthalein; consequently the reddening of an alcoholic solution of soap by phenolphthalein cannot be used alone as an indication of the presence of free alkali. K. J. P. O.

Preparation of Standard Solutions of Sulphuric Acid by Electrolysis. By DAUVÉ (*J. Pharm. Chim.*, 1902, [vi], 16, 65—66).—The strength of a solution of sulphuric acid, produced by the electrolysis of a neutral solution of copper sulphate, cannot be determined by weighing the copper deposited on the cathode, because cuprous oxide is invariably deposited along with the metallic copper (compare Hart and Croasdale, *J. anal. Chem.*, 1890, 4, 424).

H. R. LE S.

**Volumetric Estimation of Soluble Iodides.** By E. RICHARD (*J. Pharm. Chim.*, 1902, [vi], **16**, 207—209).—Ten c.c. of a 1 per cent. solution of the iodide to be estimated are mixed with 10 c.c. of a 0.5 per cent. solution of potassium iodate and 10 c.c. of a 4 per cent. solution of tartaric acid. The mixture is shaken and immediately treated with 20 c.c. of a 10 per cent. solution of disodium hydrogen phosphate, and the free iodine titrated by means of a standard solution of sodium thiosulphate. Tartaric acid is used in preference to all other acids because it has no action on chlorides or bromides in the cold. The sodium phosphate neutralises the free tartaric acid with production of sodium tartrate and sodium dihydrogen phosphate.

H. R. LE S.

**Detection of Iodine and Bromine in the Presence of Thio-sulphates.** By AUGUSTE F. LEUBA (*Ann. Chim. anal.*, 1902, **7**, 298—299).—The boiling solution is mixed with a slight excess of lead nitrate which after a few minutes precipitates the thiosulphate. Although the greater part of the iodine is also precipitated, sufficient is left in the filtrate to apply the ordinary tests for iodine; the same process also applies to the detection of bromine. Bromine, however, is best detected by adding to the solution a little sodium hydroxide and a little fluorescein, which causes an intensely red coloration.

L. DE K.

**Improved Reactions and Methods of Preparation of Ozone; Ursol D as a Reagent for Ozone.** By CARL ARNOLD and CURT MENTZEL (*Ber.*, 1902, **35**, 2902—2907. Compare this vol., ii, 352).—The violet reaction given by test papers of tetramethyldi-*p*-aminophenylmethane with ozone (*loc. cit.*) is shown to be obtained only when the ozone is quite free from acids. Traces of the latter produce a blue or bluish-green reaction. Thus ozone, prepared from barium peroxide containing nitrite, or from persulphates or sodium peroxide and sulphuric acid, gives a blue reaction, unless previously washed with alkali, or the test papers moistened with a solution of a weak base, ammonia, &c. Ozone is best recognised in aqueous solution by adding one or two drops of a methyl alcoholic solution of tetramethyldi-*p*-aminophenylmethane and 1—2 c.c. of an aqueous solution of silver nitrate or manganous sulphate. In the presence of minute traces of permanganate or cerium sulphate, which give a similar colour reaction with the test, it is necessary to add a saturated solution of ferrous sulphate before addition of the reagent. With river or well water, manganous sulphate is preferable to silver nitrate. Hydrogen peroxide can be recognised in the presence of ozone by means of a solution of benzidine and copper sulphate, which gives a blue precipitate with hydrogen peroxide, but only a reddish-yellow precipitate with ozone. It has been demonstrated by this means that, in neutral solution, ozone and hydrogen peroxide have no action on one another.

Details are given of the best methods of preparing ozone by the action of the dark electric discharge, or of phosphorus on oxygen, and by that of concentrated sulphuric acid on permanganate, persulphate, or barium or hydrogen peroxide.

It is shown that "ursol D," the reagent recommended by Chlopin (this vol., ii, 582) for detecting ozone, only gives a blue coloration in the presence of acids. Pure ozone gives a transient, pale blue coloration, rapidly becoming yellowish-brown.

K. J. P. O.

**Estimation of Sulphur in Coal and Pyrites.** By A. REITLINGER (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 457—461).—The author gives a modification of Antony and Lucchesi's method (Abstr., 1899, ii, 517) for estimating the sulphur in coal and pyrites which can be carried out in a comparatively short space of time. 0.5 Gram of the finely powdered coal is intimately mixed with 1 gram of manganese dioxide, 0.5 gram of potassium carbonate, and 0.5 gram of magnesium oxide, and the mixture heated in an inclined platinum crucible by means of a gradually increasing flame. After a quarter to a half hour's heating, the crucible is allowed to cool and then with its contents placed in a beaker of hot water to which is added 10 c.c. of concentrated hydrochloric acid; the beaker is next heated until the mass dissolves, the liquid being then neutralised with ammonia solution to precipitate the ferric hydroxide which is removed by filtering. Experiments made by the author show that by this means the silica is completely precipitated without requiring the long evaporation with hydrochloric acid. The liquid is finally heated to boiling and the sulphuric acid precipitated by means of barium chloride. The process may be still further shortened by using for the oxidation of 0.5 gram of coal, a mixture of 1.5 grams of magnesium oxide, and 1.5 grams of manganese dioxide.

The estimation of sulphur in pyrites is carried out in a similar way, a mixture of 2 grams of manganese dioxide, 1 gram of potassium carbonate, and 1 gram of magnesium oxide being employed with 0.5 gram of the mineral.

A series of parallel estimations shows that the method gives results practically identical with those obtained by the use of the much slower process of Eschka (*Chem. Zeit.*, 1892, 16, 1070). T. H. P.

**A Volumetric Method for the Estimation of Sulphuric Acid in Soluble Sulphates.** By YASUJURO NIKAIIDO (*J. Amer. Chem. Soc.*, 1902, 24, 774—778).—The method is based on the precipitation of the sulphate in alcoholic solution (60 per cent.) by *N*/10 lead nitrate solution, using potassium iodide as indicator, the yellow colour of the lead iodide becoming visible only when all the sulphuric acid has been precipitated. Free nitric or hydrochloric acid, sodium acetate or large quantities of chlorides, must not be present in the solution. In the case of the sulphates of the heavy metals (iron, zinc, &c.), a little acetic acid should be added to prevent the formation of basic sulphates. The titration must be carried out in the cold.

W. P. S.

**Estimation of Sulphuric Acid in Soils.** By C. B. WILLIAMS (*J. Amer. Chem. Soc.*, 1902, 24, 658—661).—In order to obtain trustworthy estimations of sulphur in pyrites, Lunge has found it necessary to remove the iron by means of excess of ammonia before

precipitating with barium chloride. The author now recommends the removal of the iron and alumina in solutions obtained from ferruginous soils before the estimation of the sulphates is attempted.

L. DE K.

**Quantitative Separations by Persulphates in Acid Solution.** By MAX DITTRICH and C. HASSEL (*Ber.*, 1902, 35, 3266—3271).—Manganese is completely precipitated from a slightly acid (sulphuric or nitric acid) solution by boiling with ammonium persulphate. The precipitate settles well and can easily be filtered. Ammonium persulphate is better than potassium persulphate because it decomposes more easily. Results are given which show that the method works well for the separation of manganese from magnesium, zinc, or aluminium.

The evaluation of persulphate is best carried out by heating with manganese sulphate and hydrochloric acid, conducting the chlorine evolved into potassium iodide solution, and then determining the amount of iodine separated.

J. McC.

**Volumetric Estimation of Selenium.** By K. FRIEDRICH (*Zeit. angew. Chem.*, 1902, 15, 852—856).—The selenium precipitate obtained in the usual course is returned with the filter to the beaker and boiled with 10 c.c. of ammonia and 25 c.c. (or more) of *N*/10 silver nitrate. Black silver selenide is formed and sometimes a white deposit of silver selenite is obtained which, however, redissolves on adding more ammonia. When cold, the liquid is acidified with dilute nitric acid (31.5 grams per litre) until any precipitate of silver selenite has redissolved and the excess of silver is then estimated by Volhard's thiocyanate method. One c.c. of *N*/10 silver represents 0.005914 gram of selenium. The method becomes less accurate when the amount of selenium exceeds 0.05 gram.

L. DE K.

**Behaviour of Selenious Acid in the Marsh Apparatus.** By IWAN SCHINDELMEISER (*Zeit. öffentl. Chem.*, 1902, 8, 306—309).—On adding 0.025 gram of selenious acid to the flask of a Marsh apparatus, the evolution of hydrogen practically ceased, the pieces of zinc being coated with a brown film and a flocculent, brown-red precipitate appearing in the acid solution. This precipitate was found to be a selenium-zinc compound containing from 11 to 19 per cent. of zinc. When aluminium and sodium hydroxide solutions were employed, selenious acid also caused the evolution of hydrogen to cease after a time. In none of the experiments was a mirror obtained. Selenious acid and arsenious oxide were then introduced together into a Marsh apparatus. So long as selenious acid remained in solution no arsenical mirror formed, but when the selenium had separated as a precipitate, the arsenic came over, no trace remaining in the precipitate.

W. P. S.

**Comparative Estimations of Nitrogen by the Method of the Association [of Agricultural Experiment Stations] and the Gunning-Atterberg Modification of Kjeldahl's Method.** By OSCAR KELLNER (*Landw. Versuchs-Stat.*, 1902, 57, 297—304).—The method adopted by

the Association of German Agricultural Experiment Stations consists in heating the substance for three hours with sulphuric acid, containing 200 grams of phosphoric oxide per litre, and about a gram of mercury. In the Gunning-Atterberg modification, the substance (1—2 grams) is heated for about 15 minutes with sulphuric acid (20 c.c.) and mercury (about 1 gram). Potassium sulphate (15—18 grams) is then added, and the mixture boiled for about 15 minutes after it has become colourless. The potassium sulphate may be added at the commencement in the case of substances which do not froth.

The results of a considerable number of determinations, made at Bonn, Danzig, and Hohenheim, showed that the two methods are equally trustworthy, the difference in both cases being less than 0.1 per cent. of nitrogen in 95 per cent. of the analyses.

Both potassium sulphate and phosphoric oxide quickened the decomposition, and potassium sulphate had the advantage that it does not attack the glass. In one case, it was found that the potassium sulphate contained nitrogen (0.001662 per cent.). N. H. J. M.

**Estimation of Nitric Acid in Water.** By RUDOLF WÖY (*Zeit. öffentl. Chem.*, 1902, 8, 301—304).—The following modification of Devada's method is described. Five hundred c.c. of the water are boiled in a round-bottomed flask of 800 c.c. capacity until the volume is reduced to 100 c.c. After cooling the contents of the flask to about 50°, 1 gram of an alloy, consisting of aluminium, 59 parts, copper, 39 parts, and zinc, 2 parts, is added together with 5 c.c. of alcohol and 50 c.c. of sodium hydroxide solution (about 280 grams per litre). The flask is then connected to a condenser, a bulb apparatus being placed between the two to prevent splashing over; the lower end of the condenser dips into a measured volume of standard acid. The contents of the flask are kept moderately warm for at least 30 minutes, and then distilled, 100 c.c. of distillate being collected. The excess of acid is titrated, using congo-red as indicator, and the number of c.c. of *N*/10 acid neutralised by the ammonia multiplied by 10.4, gives the milligrams of  $N_2O_5$  per litre. The acid should be standardised by distilling a known weight of ammonium chloride under the above conditions, and a blank distillation with distilled water and the sodium hydroxide should be made to correct for any ammonia contained in the latter. W. P. S.

**Detection of very small Quantities of Arsenic.** By GABRIEL BERTRAND (*Bull. Soc. Chim.*, 1902, [iii], 27, 851—854).—The author describes the precautions which must be observed in order to detect very small amounts of arsenic (1/1000—1/2000 mg.) in Marsh's apparatus. Small volumes of liquid are employed, the apparatus is first freed from air by passing a current of carbon dioxide, and the tube on which the arsenic deposit is to be obtained is of very small bore. A. F.

**Estimation of Minute Quantities of Arsenic.** By CARL TH. MÖRNER (*Zeit. anal. Chem.*, 1902, 41, 397—413).—Arsenic in quantity amounting to only a fraction of a milligram can be accurately



estimated in such substances as wall-papers, fabrics, glucose, &c., by the following process. The substance is distilled with fuming hydrochloric acid, the distillate received in dilute nitric acid and the solution evaporated to dryness. For the destruction of the organic matter, which is invariably present in this distillate, the residue, while being warmed on the water-bath, is treated with 2 c.c. of 5 per cent. potassium hydroxide (for 1 minute), 2 c.c. of 5 per cent. potassium permanganate (3 minutes), 2 c.c. of 5 per cent. sulphuric acid (3 minutes), and then with 1 c.c. of 20 per cent. tartaric acid, and warmed until colourless. The solution is then filtered, again heated, and mixed with 1 c.c. of a 5 per cent. solution of thioacetic acid. This precipitates the arsenic as trisulphide. After cooling, the precipitate is collected on a 4 cm. filter of the best filter paper and washed five times with 2 c.c. of 0.5 per cent. sulphuric acid, and three times with 2 c.c. of distilled water. The precipitate is then dissolved by pouring into the filter 2 c.c. of 0.5 per cent. potassium hydroxide solution (repeated three times), and the solution received in a flask containing 25 c.c. of *N*/100 permanganate. Oxidation to arsenic and sulphuric acids takes place instantly; the liquid is acidified with 5 c.c. of 5 per cent. sulphuric acid; a quantity of *N*/100 oxalic acid equivalent to the permanganate is added and when the precipitated manganese peroxide has been dissolved by warming, the residual oxalic acid is titrated with *N*/100 permanganate. A small correction (about 0.3 c.c.) is required for organic matter dissolved by the potassium hydroxide from the filter paper and is best estimated by making a blank experiment. In 40 test estimations with materials of the most varied character to which 0.25 mg. of arsenic was added, the result never differed by more than 0.05 mg., and in 29 of them by not more than 0.02 mg. from the quantity taken. One c.c. of *N*/100 permanganate is equivalent to 0.0536 mg. of arsenic in the form of  $\text{As}_2\text{S}_3$ . M. J. S.

**Decomposition of Ores containing much Arsenic, Iron and Lead with Sulphuric Acid.** By H. NISSENSON and F. CROTOGINO (*Chem. Zeit.*, 1902, 26, 847—849).—Ores containing sulphur and arsenic in combination with iron, lead, copper, antimony, zinc, cobalt, nickel, &c., may be rapidly decomposed by heating the finely powdered sample with strong sulphuric acid in a round-bottomed flask for a time varying from half-an-hour to three hours; the end of the reaction may be readily judged from the appearance of the mass. When cold, hot water is added which dissolves the arsenious acid and the soluble sulphates whilst the residue contains insoluble sulphates such as that of lead and compounds of antimony. The metals are then separated by well-known processes. The great advantage of the sulphuric acid treatment is that no arsenic is lost by volatilisation and also that it is obtained in a form readily precipitable by hydrogen sulphide.

L. DE K.

**Action of Boiling Hydrochloric Acid on Arsenic Acid.** By OTTO HEINER (*Analyst*, 1902, 27, 268—270).—On distilling pure concentrated hydrochloric acid, to which 0.3 per cent. of arsenic oxide had been added, cork joints being used to connect the distillation

flask and fractionating column to the condenser, arsenic could always be detected in the distillates by the hydrogen sulphide test, even when potassium permanganate had been added before commencing the distillation. Ferric chloride was also found to be reduced in the distillation flask. Using nothing but ground-glass connections, no formation of ferrous salt could be detected, and in the arsenic experiments arsenic could not be discovered in the distillates by hydrogen sulphide. The Marsh-Berzelius test, however, gave plain indications of arsenic. As every precaution had been taken to cleanse the flask and condenser from organic matter, the author considers this reduction to be due to the unavoidable presence of atmospheric dust. To prepare acid free from arsenic, it is better to add a powerful reducing agent, then distil, and only collect the distillates after all the arsenic has come over.

W. P. S.

**Estimation of Boric Acid in Margarine.** By ADOLF BEYTHIEN (*Zeit. Nahr. Genussm.*, 1902, 5, 764—766).—From 50 to 100 grams of margarine are weighed into a wide-necked flask and well shaken with 50 grams of hot water. As soon as partial separation has taken place, the contents of the flask are filtered through a dry filter. The almost clear filtrate is cooled to the ordinary temperature, and a portion (usually 40 c.c. can be obtained) is withdrawn by a pipette and neutralised with *N*/10 sodium hydroxide, using phenolphthalein as indicator. Twenty-five c.c. of glycerol are then added, and the titration completed. The *N*/10 sodium hydroxide should be standardised against a known weight of boric acid.

W. P. S.

**New Method of Organic Analysis.** By PAUL THIBAULT and A. CH. VOURNASOS (*Bull. Soc. Chim.*, 1902, [iii], 27, 895—901).—In principle, the method consists in heating the organic substance, mixed with copper oxide (or copper oxide and lead chromate), in a vessel of cast iron to which the absorption apparatus is attached; a side tube permits of a current of oxygen being passed into the vessel for the completion of the combustion. The authors claim great accuracy and expeditiousness for the method.

A. F.

**Gasometric Method for Alkalimetry.** By E. RIEGLER (*Zeit. anal. Chem.*, 1902, 41, 413—419).—The action of hydrazine sulphate on an iodate takes place according to the equation  $6\text{N}_2\text{H}_4\text{SO}_4 + 4\text{NaIO}_3 = 2\text{Na}_2\text{SO}_4 + 4\text{H}_2\text{SO}_4 + 4\text{HI} + 12\text{H}_2\text{O} + 6\text{N}_2$ , whence 1 c.c. of nitrogen (at 0° and 760 mm.) corresponds with 5.2216 mg. of iodic acid, or with 0.0297 *E* mg. of a base of which *E* is the equivalent. If, therefore, an alkali is accurately neutralised with iodic acid and the product treated with hydrazine sulphate in an azotometer, the alkali can be estimated without the use of a standard acid. The author's indicator, diazonitroaniline, can be used with ammonia as well as with the other alkalis when neutralising.

M. J. S.

**Estimation of Calcium and Magnesium in Water.** By ALBERT GRITTNER (*Zeit. angew. Chem.*, 1902, 15, 847—852).—A criticism of Clark's soap test and its modifications by Winkler, Pfeifer and others and also of Wartha's alkalimetric process for the estimation of calcium and magnesium in water.

The author could not obtain satisfactory results with Winkler's process, but thinks that good technical results may be got by a combination of Pfeifer's and Wartha's methods. L. DE K.

**Estimation of Free Anhydrous and Hydrated Lime in Cements.** By GEORGE W. MAYNARD (*Bull. Soc. Chim.*, 1902, [iii], 27, 858—882).—For the purpose of estimating the amount of free lime in cements, the author extracts the cement with pure glycerol, which has the property of dissolving the lime but not the other constituents of the cement. A. F.

**Double Ammonium Phosphates in Analysis.** By MARTHA AUSTIN (*Amer. J. Sci.*, 1902, [iv], 14, 156—158).—Dakin has proposed to substitute ammonium phosphate for microcosmic salt when precipitating zinc or manganese as double ammonium phosphates in the presence of ammonium chloride. The precipitates are first washed with a 1 per cent. solution of ammonium phosphate and then with strong, but not absolute, alcohol.

It appears from the author's investigation that the satisfactory results obtained by Dakin are due to a compensation between the increase caused by the washing with alcohol and a loss due to the slight solubility of the asbestos he has employed. When using suitable anhydrous asbestos, the process as given by the author may be safely used for the estimation of magnesium, manganese, cadmium, and zinc (Abstr., 1900, ii, 49). L. DE K.

**Quantitative Separation of Zinc and Cobalt.** By ARTHUR ROSENHEIM and ERNST HULDSCHINSKY (*Zeit. anorg. Chem.*, 1902, 32, 84—90).—In acetic acid solution, zinc sulphide can be quantitatively precipitated and treated in the ordinary manner; very little cobalt is carried down by the zinc sulphide.

Potassium cobaltinitrite precipitated from acetic acid in presence of zinc is never pure and the two metals cannot be satisfactorily separated by this means. The best separation is effected by precipitating zinc sulphide from a solution of the mixed salts to which potassium cyanide has been added in order to form potassium cobalticyanide. The separation cannot be carried out by precipitating cobalt peroxide by means of potassium persulphate from an alkaline solution because the precipitate always contains a considerable quantity of zinc hydroxide. J. McC.

**Application of Hydroxylamine and Hydrazine Salts in Qualitative Analysis. A New Separation in the Hydrogen Sulphide Group.** By EMIL KNOEVENAGEL and ERICH EBLER (*Ber.*, 1902, 35, 3055—3067).—On account of the many difficulties of the separation of the metals of group II, the authors have devised methods of separating these metals by means of hydrazine, and hydroxylamine and hydrogen peroxide. In the first process, the precipitated sulphides are dissolved in a mixture of hydrochloric and nitric acids, and, after evaporation of the excess of acid, the solution is diluted and dropped into a mixture of 20 per cent. sodium hydroxide solution and saturated

hydrazine sulphate solution. The mixture is warmed, diluted, then filtered. The precipitate may contain metallic mercury or copper, or the hydroxides of cadmium or bismuth, whilst the filtrate may contain sodium arsenate, sodium antimonate, sodium stannate, or sodium plumbate. A process is given for identifying the metals in the precipitate. In the filtrate, the lead is identified by precipitation with hydrogen sulphide, and the arsenic, antimony, and tin in the usual way.

A second method is to dissolve the sulphides in a mixture of hydrochloric and nitric acids, evaporate to dryness, and after the addition of 3—4 c.c. of nitric acid to pour into concentrated ammonia solution containing hydrogen peroxide. The precipitate obtained may contain lead as peroxide along with bismuth hydroxide and stannic acid, whilst the solution contains copper, cadmium, and mercury as soluble complex ammonium compounds and ammonium arsenate and antimonate. The precipitate is treated with sodium carbonate and a little ammonium sulphide, when the tin passes into solution. From the filtrate, mercury can be separated by a hydrazine or hydroxylamine solution, then, on addition of magnesium chloride, magnesium arsenate is precipitated. Copper is separated as thiocyanate, cadmium as sulphide, by means of ammonium sulphide, and, on acidifying, the antimony is precipitated as sulphide. The authors also describe the necessary modifications when platinum, gold, or molybdenum are present.

J. McC.

**The Lake Superior Fire Assay for Copper.** By GEORGE L. HEATH (*J. Amer. Chem. Soc.*, 1902, 24, 699—708).—The method is only suitable for native copper occurring in veins or bedded deposits, including the milled concentrates from the same, and also any oxides, carbonates, or silicates of copper, if entirely free from sulphur. The carefully taken sample (1000 grains) is mixed with fused sodium carbonate and borax (70 to 200 grains of each) and potassium hydrogen tartrate (300 to 350 grains). To rich ores, some old assay slag is added. The charge is fused in a closed crucible in a pot furnace, the latter being brought to a high temperature before introducing the crucible. The fusion requires about 20 minutes, and it is possible to tell by the eye the purity of the copper button and the waste (usually about 0.25 per cent.) in the slag. This waste is balanced by the presence of about 0.25 per cent. of iron in the button. W. P. S.

**Estimation of Copper by Potassium Permanganate.** By H. A. GUESS (*J. Amer. Chem. Soc.*, 1902, 24, 708—711).—The following method is stated to be at least as accurate as either the cyanide or iodide method for the estimation of small or fractional percentages of copper in crude ores, tailings, &c. From 1 to 5 grams of the sample are digested with aqua regia, with the addition of a few drops of sulphuric acid. The excess of acid is boiled off and the acid solution diluted and filtered. The filtrate is neutralised with ammonia, rendered just acid by a few drops of hydrochloric acid, and reduced by adding an excess of sodium sulphite. The copper is precipitated by either ammonium or potassium thiocyanate, the solution being then

boiled, and decanted on to a filter (11 cm. in diameter) as soon as the precipitate has settled. After bringing the precipitate on the filter, it is well washed with hot water, the funnel is placed over the original precipitation flask and twice filled with 10 per cent. sodium hydroxide solution; insoluble, yellow cuprous hydroxide remains on the filter, sodium thiocyanate passing through. The filter and precipitate are washed with hot water, and the filtrate, while still warm, is titrated with standardised potassium permanganate solution, after being first made decidedly acid with dilute sulphuric acid. As cuprous thiocyanate is slightly soluble, the permanganate solution should be standardised against pure copper treated as just described, and the small error arising from the action of the filter paper on the hot sodium hydroxide solution corrected for by treating an empty filter under similar conditions and titrating the filtrate.

W. P. S.

**Application of Eschka's Method to Pig Iron.** By JOHN V. R. STEHMAN (*J. Amer. Chem. Soc.*, 1902, 24, 644—649).—The author applies the principle of Eschka's sulphur estimation in coal, &c., to pig iron. Three grams of the powdered sample, of a fineness exceeding 50 mesh, are mixed in a 30 c.c. platinum crucible with 2.5 grams of basic mixture, and the whole is then covered with another 0.5 gram of the mixture. This basic mixture is composed of 2 parts of magnesium oxide and 1 part of dry sodium carbonate, or 4 parts of magnesium oxide, 1 part of sodium carbonate, and 1 part of potassium carbonate; the second mixture offers no advantage over the first. The crucible is then heated, by means of a gasoline lamp, for one hour at a full red heat. When cold, the mass is broken up with a glass rod, placed in a beaker, and extracted with hot water; 15 c.c. of bromine water are added, and the whole is boiled for 15 minutes. To the filtrate, which should be quite clear, 1.5 c.c. of hydrochloric acid are added, and, after boiling off the bromine, the sulphuric acid derived from the sulphur in the iron is then estimated as usual. Any sulphuric acid contained in the reagents should be allowed for.

If ordinary coal gas is used as the source of heat, care must be taken to prevent absorption of sulphurous fumes during the ignition. This is successfully prevented by using an asbestos board 8 inches by 4 inches; in the centre of this board and near the lower edge, a clean hole is cut of a size sufficient to admit the crucible. To the upper edge of this board is hinged, by means of a copper wire, a board of the same length, but 3 inches wide and without any hole. This shield is then placed over the tripod in such a manner that when the crucible is put into place about seven-eighths of its length projects through the board and rests on the platinum triangle. The products of combustion from the gas then pass off above and away from the crucible.

The results agree very well with those obtained by Blair's standard method.

L. DE K.

**Estimation of Iron.** By F. SEILER and A. VERDA (*Chem. Zeit.*, 1902, 26, 803—804).—The authors obtained satisfactory results in the colorimetric estimation of small quantities of iron by means of potassium ferrocyanide or potassium thiocyanate, but found that still

more correct results are got by operating as follows. The solution containing the iron as ferric chloride is diluted to 100 c.c.; of this, 10 c.c. are put into a cylinder, mixed with excess of potassium thiocyanate, and diluted to 50 c.c. Ten c.c. of the mixture are diluted with water until a clear red colour is obtained, and a solution of potassium ferrocyanide (0.97 gram per litre) is then added until the colour of the liquid turns green. Each c.c. of ferrocyanide represents 0.0002 gram of iron. If only traces of iron are present, there is no need for so much dilution.

L. DE K.

**Precipitation of Ammonium Vanadate by Ammonium Chloride.** By FRANK A. GOOCH and R. D. GILBERT (*Amer. J. Sci.*, 1902, [iv], 14, 205—210).—The authors have thought it necessary to make fresh experiments to determine whether ammonium metavanadate is insoluble in a completely saturated solution of ammonium chloride, and have found that in the presence of a little free ammonia such is the case. The precipitate must be washed with a saturated solution of ammonium chloride, and the vanadium may then be estimated in the residue by any appropriate means. Gibbs's process (*Amer. Chem. J.*, 1883, 5, 371), based on the precipitation of vanadium as ammonium vanadate and titration of this with permanganate, may therefore be safely used, or Browning's iodometric process may be employed.

L. DE K.

**Precipitation of Ammonium Vanadate by Ammonium Chloride.** By ARTHUR ROSENHEIM (*Zeit. anorg. Chem.*, 1902, 32, 181—182).—The precipitation of ammonium vanadate by ammonium chloride is satisfactory for pure vanadate solutions, but does not give sufficiently accurate results for the quantitative separation of vanadic and tungstic acids.

J. MCC.

**Solubility of the Sulphides of Arsenic, Antimony, and Tin.** By WILLIAM R. LANG and C. M. CARSON (*J. Soc. Chem. Ind.*, 1902, 21, 1018. Compare this vol., ii, 530).—Continuing their experiments, the authors tabulate the solubilities of the sulphides in various strengths of hydrochloric acid under different conditions and temperatures. They find that arsenious sulphide is insoluble in hydrochloric acid of sp. gr. 1.16 if hydrogen sulphide is passed into the mixture to saturation. Antimony trisulphide is soluble in a mixture of hydrochloric acid of sp. gr. 1.16 (50 parts) and water (18 parts), even when the solution is completely saturated with hydrogen sulphide. Stannous sulphide is soluble in hydrochloric acid slightly more dilute than that required to dissolve antimony trisulphide.

To separate arsenious sulphide from antimony and tin sulphides, the mixture should be treated with hydrochloric acid diluted with not more than one-third its volume of water, and then saturated with hydrogen sulphide. Arsenious sulphide remains insoluble, and may be removed from the other two sulphides by filtration and washing with a mixture of hydrochloric acid and water (50:18) or with acid containing hydrogen sulphide.

W. P. S.

**Quantitative Separation of Zirconium and Iron.** By ALEXANDER GUTBIER and G. HÜLLER (*Zeit. anorg. Chem.*, 1902, 32, 92—95).—To the solution containing the iron and zirconium, ammonia is added, and the precipitate of mixed ferric and zirconium hydroxides is filtered off, dried, ignited, and weighed. The mixture of ferric and zirconium oxides is ignited in a current of hydrogen; the ferric oxide is reduced to metallic iron but the zirconium oxide is not affected. From the decrease in weight, the amount of iron present can be calculated. Experimental numbers are given which show that the method is accurate.

The method can also be used to determine iron and aluminium together, since aluminium oxide suffers no reduction when heated in hydrogen. J. McC.

**Estimation of Platinum, Gold, and Silver in Alloys.** By PERCY A. E. RICHARDS (*Analyst*, 1902, 27, 265—268).—The following methods were found to give the most accurate results.

*a. Alloys containing Platinum and Silver only.*—About 0.3 gram of the alloy is heated with 10 c.c. of pure sulphuric acid until all apparent action has ceased. When cold, the acid is decanted into a beaker containing cold water, and the residue of metal again treated with sulphuric acid. After pouring off this acid (adding it to the first), the residue of platinum is washed with water (the washings being added to the silver sulphate solution), transferred to a crucible, dried in the air-bath, and weighed. The platinum retains to some extent its original shape, but has a blistered appearance. The silver in the acid filtrate is estimated by the thiocyanate method.

*b. Alloys containing Gold, Platinum, and Silver.*—The alloy is treated with sulphuric acid as just described, the residue of gold and platinum being washed, dried, and weighed as a check. This residue is then dissolved in nitro-hydrochloric acid, concentrated to a small bulk, and the platinum separated as ammonium platinichloride. The gold in the filtrate is precipitated by ferrous sulphate, washed, dried, and weighed.

*c. Alloys containing Gold, Platinum, Silver, and Tin.*—The silver and tin are separated by the sulphuric acid treatment just described, the silver being afterwards titrated in the acid solution and the tin taken by difference. Fair results are also obtained by heating the alloy in a current of chlorine, the tin chloride being volatilised and estimated by difference. Attempts to collect the tin chloride in water were not successful. W. P. S.

**Estimation of the Reducing Power of Natural Waters.** By LUDWIG W. WINKLER (*Zeit. anal. Chem.*, 1902, 41, 419—426).—To estimate the amount of permanganate reduced by a natural water, the author prefers to boil the water for 10 minutes with strongly alkaline permanganate, partly because the oxidation of the organic matter is more complete in alkaline than in acid solutions, and partly because with acid solutions percussive ebullition is scarcely to be avoided. To prepare the standard permanganate, 50 grams of sodium hydroxide (purified by alcohol) are dissolved in 500 c.c. of water, boiled for a

quarter of an hour, and cooled; 0.8 gram of permanganate is added, and the whole made up to 500 c.c. For use, this solution is diluted five-fold, and standardised with  $N/100$  oxalic acid. When 10 c.c. of this solution, mixed with 100 c.c. of purified distilled water, are boiled for 10 minutes, a loss of oxygen equal to 0.175 c.c. takes place. As  $N/100$  oxalic acid is employed for estimating the unreduced permanganate, special experiments on the permanence of such a solution were made. When prepared with  $N/10$  sulphuric acid instead of with water,  $N/100$  oxalic acid loses only 0.3 per cent. of its strength in 6 months.

M. J. S.

**The Significance of Phosphates in Natural Waters.** By A. G. WOODMAN (*J. Amer. Chem. Soc.*, 1902, 24, 735—743).—The conclusion arrived at is that the presence of phosphates in water in any quantity indicates pollution. Analyses of 42 samples of water, including estimations of phosphoric acid, confirm this statement. The amounts of phosphoric acid generally varied with the quantities of nitrates and chlorides, although exceptions were found. Less than 1 part of phosphoric oxide per million is considered to be the limit for unpolluted waters.

W. P. S.

**Fractional Combustion of Hydrogen, Carbon Monoxide, and *iso*Pentane.** By K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 461—465).—The author has carried out a number of experiments with mixtures of hydrogen and *isopentane* and of hydrogen and carbon monoxide, the results obtained showing that Winkler's method of fractional combustion in presence of palladinised asbestos is totally inapplicable to the analysis of natural gas. It is also found that, in presence of palladinised asbestos: (1) Pure hydrogen undergoes complete combustion at 80°, carbon monoxide at about 290°, and *isopentane* at a temperature beyond 315°. (2) Nitrogen and other indifferent gases are without influence on the temperature of combustion of hydrogen. (3) An admixture of carbon monoxide and *isopentane* considerably raises the temperature of combustion of hydrogen. (4) If hydrogen be mixed with an equal volume of *isopentane*, it will burn slowly at 200°, 1.6 to 9.2 per cent. of the *isopentane* also undergoing combustion at the same time. (5) The speed of the reaction in the combustion of *isopentane* is very small, and in order that the gas may be completely burnt it must be drawn many times over the strongly heated asbestos. (6) The above observations regarding *isopentane* also hold for carbon monoxide.

T. H. P.

**Recognition of Aromatic Hydrocarbons.** By EDUARD LIPPMANN and ISIDOR POLLAK (*Monatsh.*, 1902, 23, 670—681).—On addition of concentrated sulphuric acid and a few drops of benzylidene chloride, the following hydrocarbons give characteristic colour reactions: anthracene, malachite-green; naphthalene, rosaniline; benzene, light yellow; toluene, light yellow; phenanthrene, carmine; xylene, orange; triphenylmethane, feeble yellow; diphenylmethane, brick-red; stilbene, blue-green;  $\psi$ -cumene, orange-red; cymene, orange; pyrene, emerald green becoming deep blue; picene, olive-



green, the colour forming slowly; dibenzylanthracene, light green; acenaphthene, intense dark blue; chrysene, light yellow becoming light green, and finally dark olive-green.

Benzene, toluene, xylene,  $\psi$ -cumene, and cymene give the characteristic colour with sulphuric acid alone. G. Y.

**Examination of Alcoholic Liquids for Methyl Alcohol.** By N. SCHOORL (*Zeit. anal. Chem.*, 1902, 41, 426—428).—The author does not agree with Habermann and Oesterreicher that pure methyl alcohol reduces permanganate more rapidly than ethyl alcohol (this vol., ii, 110), but attributes their result to the presence of traces of acetone and other easily oxidisable substances in the methyl alcohol which they employed. The Riche-Bardy and Trillat-Wolf methods are the only trustworthy ones for detecting small quantities of methyl alcohol in ethyl alcohol. M. J. S.

**Presence of Arsenic in Glycerol.** By LÉONCE BARTHE (*J. Pharm. Chim.*, 1902, [vi], 16, 52—55).—Glycerol which is free from arsenic may, on treatment with zinc and hydrochloric acid, evolve a gas which reduces silver nitrate. This test is therefore not a trustworthy one for the detection of arsenic in glycerol. Bougault's method (this vol., ii, 530) is very satisfactory and is applicable to the detection of arsenic in glycerol. H. R. LE S.

**Diagnosis of Pentosuria.** By MANFRED BIAL (*Chem. Centr.*, 1902, ii, 295; from *Deutsch. med. Woch.*, 28, 253—254).—Two or three c.c. of the urine suspected to contain pentose are mixed with 4—5 c.c. of a solution containing 1—1.5 grams of orcinol in 500 c.c. of fuming hydrochloric acid, and then with 25 drops of a 10 per cent. solution of ferric chloride. After heating until bubbles just begin to form, the liquid either at once deposits a green colouring matter or turns green on cooling after 15—20 seconds. The process indicates the presence of pentose, but not that of glycuronic acid. L. DE K.

**Pentoses in Urine.** By ERNST KRAFT (*Chem. Centr.*, 1902, ii, 482—483; *Pharm. Zeit.*, 47, 522).—The author recommends the process used by Bial (see preceding abstract). 0.05 per cent. of pentose may be detected by it. L. DE K.

**Capillary Constants of Sugar Solutions.** By A. DÉMICHEL (*Ann. Chim. anal.*, 1902, 7, 335—337).—A recalculation of the table constructed by the German Committee on Standard Weights for the correction of the specific gravity of sugar solutions owing to the capillary action of the liquid so as to suit the French requirement of knowing the amount of sugar in 100 c.c. and not in 100 grams of the solution. L. DE K.

**The Phenylhydrazine Test for Sugar.** By ALBERT B. LYONS (*Pharm. Rev.*, 1902, 20, 155—158).—A criticism of the various modifications of the phenylhydrazine test for dextrose in urine proposed from time to time.

In some cases, the author thinks it advisable to first remove urates and phosphates. To 8 c.c. of the urine are added 1 c.c. of *N*-barium chloride and a few drops of *N*-potassium hydroxide. After filtering, 0.2 gram of sodium carbonate is added and the liquid boiled and again filtered. To 5 c.c. of the filtrate 2 c.c. of acetic acid are added and the test with phenylhydrazine may then be applied. L. DE K.

**Estimation of Sugar by Fermentation.** By ALBERT B. LYONS (*Pharm. Rev.*, 1902, 20, 104—108).—The saccharine liquid containing from 0.2 to 1.5 grams of sugar is mixed with 2 grams of compressed yeast and introduced into a 50 c.c. fermentation flask which is then quite filled with water. The carbon dioxide is collected in a graduated cylinder, which it enters from above, and to prevent absorption the surface of the water is covered with paraffin oil.

The liquid is allowed to ferment for at least 24 hours at 25—30°. An amount of carbon dioxide equal in volume to the liquid should be added to that collected in the cylinder. If the amount of sugar is very small, the carbon dioxide may practically all remain in solution; in such a case, a known weight of sugar should be added. In accurate analyses, the precise amount of carbon dioxide evolved from a known weight of sugar and the amount retained by the liquid may easily be ascertained by direct experiment. The process is particularly recommended for the estimation of sugar in urine. L. DE K.

**Testing for Mannose.** By FRANCIS H. STORER (*Bull. Bussey Inst.*, 1902, 3, 13—45).—Twenty grams of finely powdered wood are boiled with 200 c.c. of 5 per cent. hydrochloric acid for three hours, filtered, and neutralised with sodium hydroxide solution (1:8). One c.c. of the solution is then treated with 12 drops of a solution obtained by dissolving 0.5 gram of phenylhydrazine hydrochloride in 5 c.c. of water and adding 0.3245 gram of sodium acetate. Or a mixture of phenylhydrazine (1 c.c.), glacial acetic acid (2 c.c.) and water (10 c.c.) may be employed. After two hours, or, if the quantity of hydrazine is small, after being left overnight, the mixture is examined microscopically. Full details respecting the mode of applying the method are given and the behaviour of dextrose towards phenylhydrazine is also described. A number of experiments were made in connection with the lead acetate test.

Mannose was found in the trunk-wood of sugar-maple trees, but not in the wood of the grey birch, poplar, and willow. It occurs in orange-peel (not in the seeds), in the artichoke roots, in horse chesnuts, and in the storage-roots of chicory, dandelion, and asparagus. The seeds of white pine and Norway spruce contain only a small amount of mannose, whilst the wood of these and other pines contains it in considerable quantity. N. H. J. M.

**Analyses of Honey.** By R. RACINE (*Zeit. öffentl. Chem.*, 1902, 8, 281—286).—Thirty-nine analyses are given of samples of pure and adulterated honey. Each analysis includes an estimation of the water (dry solids), total sugars, ash, specific gravity, and polarisation of the sample. The principal adulterants detected were invert sugar,

"starch syrup," molasses, and water. The specific gravity does not always indicate the presence of water in "watered" samples; it is better to estimate the dry solids directly for this purpose.

W. P. S.

**Estimation of Starch in Commercial Starches and Flours.** By E. GIANTURCO (*Rev. intern. Falsific.*, 1902, 15, 97—100).—The starch is first washed with distilled water to remove soluble matters, and is then allowed to dry at the ordinary temperature. About 2.5 grams are then well stirred in a beaker with 150—200 c.c. of water, 15 c.c. of a solution of alum (of such strength that each c.c. corresponds with 0.01 gram of aluminium hydroxide) are added, and the mixture is precipitated with a slight excess of ammonia. The precipitate is collected on a tared filter, thoroughly washed with the least possible quantity of water, dried at 100°, and weighed. From the weight found, the known quantity of aluminium hydroxide present is subtracted, the result being starch.

In the case of flour, about 3 grams are placed in a small china basin and formed into a dough by adding a small quantity of water. The lump of dough is then kneaded under a jet of water until all starch has been removed. The washings containing the starch in suspension are precipitated as above.

W. P. S.

**The Composition and Analysis of Starch Syrups.** By MAX HONIG (*Zeit. Nahr. Genussm.*, 1902, 5, 641—653).—Commercial starch syrups contain, besides dextrose, two groups of dextrins. One group consists of erythrodestrin and achroodestrin; these may be separated from starch syrup by precipitation with 87 per cent. alcohol (König's method) and then from each other by fractionation from alcohol. The author separates them from the syrup by treating 100 c.c. of a solution containing not more than 1 per cent of dextrose in a 200 c.c. graduated flask with 50 c.c. of saturated barium hydroxide solution. Sufficient 95 per cent. alcohol is then added to make the volume up to 200 c.c. after cooling and shaking. The dextrins are precipitated whilst the dextrose remains entirely soluble. The other group consists of dextrins which are soluble in alcohol, as are also the barium salts, which remain in solution with the dextrose in the above described method of separation. They may be separated from dextrose by fermentation of the filtrate. A scheme for the analysis of starch syrups is also given, and includes the estimation of: (1) The dry solids, by evaporating 50 c.c. of a solution containing 10 grams of syrup in 500 c.c. of water, and drying the residue under reduced pressure for 4 hours at 100°; (2) ash; (3) the cupric reducing power of a 10 per cent. solution of the syrup, by Soxhlet's method; (4) the cupric reducing power of the solution after the separation of the dextrins; (5) the cupric reducing power of an inverted portion of the original solution; and (6) the cupric reducing power of the inverted filtrate from the dextrin precipitate.

W. P. S.

**Estimation of Formaldehyde.** By A. PFAFF (*Chem. Zeit.*, 1902, 26, 701).—The solution of formaldehyde (containing about 0.4 per

cent.) is digested in a closed flask for one hour with a known volume of solution of hydrazine and the unabsorbed hydrazine is then titrated with *N*/10 sulphuric acid using methyl-orange as indicator; 1 mol. of sulphuric acid neutralises 2 mols. of hydrazine. Two mols. of formaldehyde absorb 1 mol. of hydrazine. The test-analyses agree very well with those obtained with Romyn's iodometric method (Abstr., 1897, ii, 166).  
L. DE K.

**Detection of Hydrogen Cyanide in Presence of Thiocyanic, Hydroferrocyanic, and Hydroferricyanic Acids, and their Salts.** By LOUIS E. PREISS (*Amer. Chem. J.*, 1902, 28, 240—241).—After removal of the heavy metals and alkaline earths by boiling with sodium carbonate, potassium hydroxide and aluminium filings are added to the solution, which is then left until the whole of the ferri-cyanide has been reduced. The solution is now acidified with hydrochloric acid, and excess of mercuric chloride is added in order to precipitate the hydroferrocyanic acid. The filtrate is made alkaline with potassium hydroxide and filtered; the clear solution is boiled with solution of ferrous sulphate, and again filtered. Hydrochloric acid and ferric chloride are added, and the iron thiocyanate is decolorised by means of mercuric chloride whereby the precipitate of Prussian blue is rendered visible.  
E. G.

**Iodometry of Thiocyanic Acid.** By ALFRED THIEL (*Ber.*, 1902, 35, 2766—2768. Compare Rupp and Schied, this vol., ii, 538).—Potassium thiocyanate, dissolved in a cold aqueous solution of sodium hydrogen carbonate, is digested for 4 hours with excess of standard iodine solution in a loosely stoppered bottle. The mixture is then treated with excess of hydrochloric acid, the cyanogen iodide formed in the first reaction being destroyed in the acid solution in accordance with the following equation:  $\text{CNI} + \text{HI} = \text{HCN} + \text{I}_2$ . The product is now titrated with standard thiosulphate solution, employing starch as indicator in the ordinary way. The amount of free iodide destroyed is a measure of the thiocyanate present,  $\text{KCNS} + 3\text{I}_2 + 4\text{H}_2\text{O} = \text{KI} + 5\text{HI} + \text{H}_2\text{SO}_4 + \text{HCN}$ .  
G. T. M.

**Estimation of Uric Acid in Urine.** By ADOLF JOLLES (*Zeit. physiol. Chem.*, 1902, 36, 39—41).—The author states that the unsatisfactory results obtained by Matrai (this vol., ii, 541) were due to his not having followed the method as originally described.  
W. P. S.

**Estimation of Uric Acid by Jolles's Process.** By ALFRED WOGGINZ (*Chem. Centr.*, 1902, ii, 666—667; from *Oesterr. Chem. Zeit.*, 5, 319—320).—Jolles's process (Abstr., 1900, ii, 450) is recommended. If a somewhat excessive amount of permanganate has been used, the quantity of alkaline hypobromite should be increased by 5 or 10 c.c.  
L. DE K.

**Oxidation and Estimation of Uric Acid and Urates.** By JAMES F. TOCHER (*Pharm. J.*, 1902, [iv], 15, 161—166).—When a dilute solution of uric acid is oxidised with acid permanganate, carb-

amide and alloxan are produced. Alloxan may be readily detected by the deep rose-red coloration produced when it is warmed with dilute ammonia, and which is changed to purple by sodium or potassium hydroxide. The variable results obtained by Hopkins's method of estimating uric acid are mainly due to the presence of alloxan formed during the reaction; if, however, the titration is carried out in a cold, very dilute solution, and the end reaction is taken at the point at which the colour persists for about 15 seconds, the Hopkins factor is trustworthy. Constant results cannot be obtained by boiling the solution of uric acid with excess of alkaline permanganate and titrating back. When uric acid is boiled for 2 minutes with solution of chromic acid, it is completely converted into carbamide and carbon dioxide; in a concentrated solution of chromic acid, however, a small portion of the carbamide may be converted into ammonia. The carbamide produced is estimated by means of hypobromite in a modified Doremus tube.

In the analysis of urine, the uric acid is precipitated as ammonium urate and oxidised with chromic acid as described above. In clinical work, a sample of the urine may be oxidised with chromic acid and the total nitrogen estimated by the hypobromite method, the nitrogen due to the carbamide being estimated in another portion from which the uric acid has been precipitated as barium urate.

An appendix to the paper contains a summary of the various methods for the estimation of uric acid which have been suggested by previous workers.

E. G.

**Estimation of the Acidity of Urine by Calcium Succrate.** By J. DE GIRARD and J. VIRET (*Bull. Soc. Chim.*, 1902, [iii], 27, 892—895. Compare Joulie, *Abstr.*, 1898, ii, 315).—The author finds that when calcium succrate is added to a solution of an acid phosphate of an alkali metal, dicalcium phosphate and an alkali phosphate are formed, whilst a portion of the original acid phosphate remains in the solution, which also has an acid reaction. For this reason, calcium succrate cannot be employed to estimate the acidity of urine.

A. F.

**The Occurrence of Salicylic Acid in Natural Wines.** By KARL WINDISCH (*Zeit. Nahr. Genussm.*, 1902, 5, 653—662).—The author was unable to detect the presence of salicylic acid in grapes of the 1901 vintage in Germany, and comes to the conclusion that it may be present in one year and not in another. That it is sometimes present is proved by the investigations of others (Ferreira da Silva and Mastbaum). The amount which has been found is extremely small, and is not detected by the ordinary method of testing wine for added salicylic acid.

W. P. S.

**Rapid Method for the Analysis of Soaps.** By FERNAND TELLE (*J. Pharm. Chim.*, 1902, [vi], 16, 121—125).—The soap (2 grams) is dissolved in hot water, 10 c.c. of *N*-hydrochloric acid are added, the fatty acids extracted with ether, and weighed. In the aqueous solution, the excess of hydrochloric acid is titrated, and from the result the total alkali deduced. The uncombined alkali hydroxide or carbon-

ate in the soap is estimated by a modification of Divine's method (Abstr., 1900, ii, 759), in which approximately  $N/10$  oleic acid is used in place of stearic acid.

H. R. LE S.

**Estimation of Fat in Milk by means of the Refractometer.** By SIGMUND HALS and HARALD GREGG (*Milch Zeit.*, 1902, 31, 433—436).—Wollny's refractometric method was compared with the Adams process for the estimation of fat in milk. The results of numerous analyses by both methods show that the percentages of fat found by the refractometer in all cases agree very accurately with the amount as determined by the Adams process. Milk, with and without preservatives, which had been kept for from 3 to 5 weeks, gave slightly lower results by the Wollny method, the difference averaging  $-0.06$  per cent. Wollny's method as used in these experiments was as follows: 20 c.c. of milk were shaken with 1 drop of copper chloride solution (238 grams per litre) and 3 drops of glacial acetic acid for 15 minutes at a temperature of  $17.5^{\circ}$ . One c.c. of a solution containing 250 grams of potassium hydroxide, 500 c.c. of water, 250 c.c. of glycerol, and 100 grams of copper carbonate was added, and then 4 c.c. of ether previously saturated with water at  $17.5^{\circ}$ . The mixture was shaken for 15 minutes and subjected to centrifugal action, the refraction of the ethereal fat solution being then determined. Naumann's modification of this method was not found to give accurate results in the case of fresh skimmed milk, where the amount of fat is low, but with sour milk it worked more satisfactorily. W. P. S.

**Analysis of Butter Fat and the Relation between the various Constants of the same.** By PAUL BEHREND and H. WOLFS (*Zeit. Nahr. Genussm.*, 1902, 5, 689—719).—The butters examined were obtained from the milk of separate cows, each butter fat being analysed separately. From the averages of the results obtained it is seen that, to a certain extent, there is a relation between the various analytical values. The Reichert-Meissl numbers of the fats decreased as the melting point rose, and the latter approximately increased in proportion with the amount of insoluble fatty acids. The Reichert-Meissl numbers also diminished as the refractometer values increased. Little relation exists between the refractometer value and the melting point. The iodine values increased with the refractometer readings, the Köttstorfer values at the same time showing a decrease. The Köttstorfer and Reichert-Meissl numbers increased as the iodine values and insoluble acids decreased.

W. P. S.

**The Unsaponifiable Substances in Butter Fat.** By ARTHUR KIRSTEN (*Zeit. Nahr. Genussm.*, 1902, 5, 833—856).—The unsaponifiable matter found in butter fats consists principally of cholesterol, with small quantities of lecithin and yellow colouring substances. The cholesterol is best separated and estimated by Bömer's method; 10 grams of the butter are saponified with an alcoholic solution of potassium hydroxide, and the dilute soap solution thoroughly extracted with ether. After distilling off the latter, the residue is again treated with potassium hydroxide solution and extracted with ether. The

ethereal solution is shaken with 5 per cent. potassium hydroxide solution, the latter being afterwards extracted with ether, and the united extracts washed with water and filtered. The final residue from the ether is dried at 100° and weighed, the weight giving the amount of "crude" cholesterol in the fat. A number of estimations of the latter are given, the results showing that the quantity varies slightly according to the period of lactation. At the commencement of lactation, the average amount of "crude" cholesterol is 0.375 per cent., rising at the end to 0.50 per cent. W. P. S.

[Detection of Margarine.] By FRANZ UTZ (*Chem. Zeit.*, 1902, 26, 730—731).—A series of experiments which proves that under certain, as yet unknown, conditions the active principle of sesamé oil may pass into the milk and consequently into the butter prepared therefrom and then cause the Baudouin or Soltsien reactions, which have lately been recommended for the safe detection of margarine in butter. It must be remembered that in some countries margarine always contains an admixture of sesamé oil as prescribed by law.

The quantity introduced seems, however, to be so trifling that the Reichert-Meissl number and the refraction of the butter are not sensibly affected when the cows have been partially fed on sesame cakes. L. DE K.

Refractive Indices of Salad Oils—Correction for Temperature. By L. M. TOLMAN and L. S. MUNSON (*J. Amer. Chem. Soc.*, 1902, 24, 754—758).—Using a Zeiss butyro-refractometer, it was found that the correction for change in the refractive index for 1° amounted to 0.000365 for ordinary fats and oils (cotton, olive, poppy-seed, sunflower, rape, mustard, black mustard, lard, pea-nut, and sesamé). The change in the refractive index for variation of temperature being more constant than the change in scale divisions, it is better to calculate the scale reading into the refractive index, make the above correction, and recalculate into scale divisions. For corrections of a few degrees, the formula  $R = R' - X(T - T')$  may be employed,  $R$  = reading corrected to  $T$ ,  $R'$  = reading at  $T'$ ,  $T$  = desired temperature,  $T'$  = temperature at which reading was made and  $X$  = change in scale division caused by change of temperature for 1°. For butters which read from 40—50° on the scale,  $X$  = 0.55; for oils reading from 60—70°, it is 0.58; and from 70—80° it is 0.62. W. P. S.

The Influence of the Growth of Mould on the Chemical Composition of Oleomargarine and Butter. By CHARLES A. CRAMPTON (*J. Amer. Chem. Soc.*, 1902, 24, 711—719).—About 50 samples of margarine, which had been kept in glass-stoppered bottles for 2 years, were re-examined at the end of this time. Many of the samples had become permeated with a growth of dark green mould, a (probably undescribed) species of *Coniothecium*. The refractive indices of the samples varied to a considerable extent, being particularly low in those showing the strongest growth of mould. The mouldy samples also gave much lower Reichert-Meissl figures as compared with a

sample of the original fat which had not become mouldy, and the specific gravities were unusually low.

An analysis of a sample of mouldy butter confirmed the statements of Hanuš and Stocký that the growth of moulds produces a decrease in the Reichert-Meissl figure (Abstr., 1900, ii, 772). The conclusions are that, in the case of edible fats, where the presence of nitrogenous and other non-fatty matters afford a medium for the growth, the greater part of the changes included under the general term "rancidity" is due to the action of micro-organisms or to the enzymes resulting from their development. The results obtained in the experiments with the oleomargarines are explained by the author, his explanations agreeing with those of König, Spieckermann, and Bremer (Abstr., 1901, ii, 676).  
W. P. S.

**Microchemical Analysis of Alkaloids.** By M. EMM. POZZI-ESCOT (*Ann. Chim. anal.*, 1902, 7, 337—338. Compare Abstr., 1901, ii, 485).—A reply to Surre (this vol., ii, 543), who has applied the process previously used by the author.  
L. DE K.

**New Reactions for Quinine and Quinidine.** By EDUARD HIRSCHSOHN (*Chem. Centr.*, 1902, ii, 540; from *Pharm. Centr. Halle*, 43, 367—368).—Neutral solutions of quinine and quinidine hydrochloride or sulphate turn a raspberry-red colour when boiled with a drop of a solution containing 2 per cent. of hydrogen peroxide and 10 per cent. of copper sulphate and thus behave like a solution of aloin. The colour gradually changes to violet-blue and finally to green. In similar circumstances, thalline sulphate or tartrate give an onion-red, kairine an intensive blue, and asparagine a light blue colour. All the other alkaloids, glucosides and bitter substances which have been investigated by the author are not coloured at all or only turn pale yellow or brownish. Free acids and alcohol interfere with the reaction. The test still shows in a dilution of 1 to 10,000. L. DE K.

**Separation of Brucine from Strychnine.** By ALBERT B. LYONS (*Pharm. Rev.*, 1902, 20, 253—255).—The process is intended for the assay of nux vomica extract. The mixed strychnine and brucine obtained in the ordinary way is treated with dilute (10 per cent.) sulphuric acid, U.S.P., using 1 c.c. of acid for every 0.015 gram of the alkaloidal mixture. It was found that in these circumstances 1 c.c. of acid dissolves only 0.00175 gram of strychnine, so that the bulk of this remains as insoluble sulphate, whilst the brucine is practically all dissolved.

After collecting the insoluble matter on a very small filter and washing with a few drops of acid, the strychnine may be recovered by shaking the sulphate with ammonia and chloroform; the latter, on evaporation, yields the fairly pure alkaloid. If it is desired to avoid making a correction for the slight solubility of strychnine, an acid saturated with the alkaloid may be used. This may be prepared by adding to 100 c.c. of a 10 per cent. sulphuric acid 0.275 gram of brucine, and 0.225 gram of strychnine, and filtering after an hour. The addition of brucine is necessary, as it increases the solubility of the strychnine.  
L. DE K.



**Assay of Opium.** By A. B. STEVENS (*Pharm. Archiv*, 1902, 5 41—45. Compare Abstr., 1901, ii, 631).—Four grams of the finely powdered sample are triturated in a mortar with 2 grams of freshly burnt calcium oxide and 10 c.c. of water; another 19 c.c. of water are added, and the whole is frequently stirred for half an hour. Fifteen c.c. of the filtrate are then placed in a 60 c.c. bottle, 4 c.c. of alcohol and 10 c.c. of ether are added, and the whole is well shaken. Half a gram of ammonium chloride is next added, and after shaking for half an hour the whole is set aside in a cold place for 12 hours. The supernatant ether is then poured off into a funnel closed with a plug of absorbent cotton, and the bottle is rinsed with another 10 c.c. of ether. The contents of the bottle are poured into the funnel, and both crystals in the funnel and bottle are washed with water saturated with morphine, until the washings are colourless. The funnel is now placed over the bottle, the cotton lifted with a glass rod drawn out to a curved point, and the crystals are rinsed into the bottle with 12 c.c. of  $N/10$  sulphuric acid; the cotton is then also put into the bottle, which is then corked and well shaken. After rinsing both cork and funnel with water the excess of acid is neutralised by  $N/40$  potassium hydroxide. The number of c.c. of  $N/10$  acid consumed multiplied by 1.5038 gives the percentage of morphine in the sample; to this must be added an extra 1.12 per cent. to compensate for morphine remaining in solution.

L. DE K.

**Evaluation of Ipecacuanha Root.** By GUSTAV FRERICHs and N. DE FUENTES TAPIS (*Arch. Pharm.*, 1902, 240, 390—423).—The authors have analysed the hydrochlorides of emetine and cephaeline, and found the same composition as Paul and Cownley (Abstr., 1896, i, 192; *Amer. J. Pharm.*, 1901, 73, 57, 107); they incline towards the formulæ adopted by the latter. Cephaeline melts at  $119^{\circ}$  when all the solvent has been driven off from it.

An historical account is given of the various methods proposed for the evaluation of ipecacuanha root, and the methods are examined critically. Preference is given to the following ones, which are slight modifications of those of Keller (Abstr., 1893, ii, 397; 1894, ii, 263). It is thought that a determination of the amount of emetine and cephaeline together is sufficient, as the amount of psychotrine (Paul and Cownley, *Amer. J. Pharm.*, 1901, *loc. cit.*) is relatively very small; moreover, the colour caused by the presence of psychotrine renders impossible a titration of the alkaloids with iodeosin as indicator. The weights of the two alkaloids which combine with  $1HCl$  being respectively 248 and 234, 1 c.c. of  $0.1N$  hydrochloric acid may be taken, without serious error, as corresponding with 0.0241 gram of alkaloid. Psychotrine is not dissolved by ether, and even when ether-chloroform is used, it is not dissolved when sodium carbonate has been employed to set free the alkaloids.

**Volumetric.**—Shake 6 grams of the powdered root with 60 grams of ether, add 5 c.c. of ammonia solution (10 per cent. ?) or 5 c.c. of sodium carbonate solution (1 : 3), and shake at intervals during an hour. Add 10 c.c. of water, shake, filter off 50 grams of the ether, concentrate it to half its bulk, and shake it with 10 c.c. of  $0.1N$  hydrochloric acid. Filter

the acid, shake the ether twice with 10 c.c. of water, running this wash-water through the same filter into the acid extract, dilute to about 100 c.c., add so much ether that a layer 1 cm. or so deep remains on the surface of the liquid after shaking, then add 5 drops of iodeosin solution (1:250), and titrate with 0.1*N* potassium hydroxide. Multiply the net number of c.c. neutralised by the alkaloid by 0.482; the result is the percentage of alkaloid in the root.

*Gravimetric.*—This method is to be preferred when an evaluation of the drug has to be performed only occasionally. The 50 grams of ethereal solution mentioned above are shaken with 5 c.c. of dilute hydrochloric acid and 10 c.c. of water, and the aqueous extract is removed to another separating funnel; the ether is then extracted twice in succession with 10 c.c. of water, and the extracts are removed to the same funnel. To the acid liquid, 5 c.c. of ammonia solution are added and the mixture is shaken with 50 grams of ether; 40 grams of the ethereal extract are evaporated in a tared flask and the residue dried at 100° and weighed; 25 times this weight gives the percentage of emetine and cephaeline together in the sample. It is possible to check the result by dissolving the residue in 5 c.c. of 0.1*N* hydrochloric acid, adding water, ether, and iodeosin, and titrating back with 0.1*N* potassium hydroxide; the end-point is obscured, however, by a discoloration resulting from the slight decomposition which the alkaloids undergo when dried. A certain assurance against adulteration may be obtained by testing qualitatively for cephaeline; dissolve the residue in Fröhde's reagent, and add a particle of sodium chloride, when dark blue coloration will appear if cephaeline is present.

A determination of the total amount of emetine and cephaeline suffices for most practical purposes. If the separate amounts are required, the determination must be repeated, the cephaeline being removed from the ethereal solution by shaking it three times with about 10 c.c. of aqueous sodium hydroxide, and the residual emetine determined; the cephaeline is determined by difference. To estimate the psychotrine, make a third determination, extracting the alkaloids with ether-chloroform, and subtracting from the total weight of alkaloids so found the weights of emetine and cephaeline. C. F. B.

**Vintage Musts and Liqueur Wines: their Specific Characters and Analysis.** By CARI-MANTRAND (*Bull. Soc. Chim.*, 1902, [iii], 27, 822—829).—To distinguish between the fresh grape juice to which alcohol has been added and true liqueur wines, the author has made a number of analyses, and finds that the weight of dry extract, after subtraction of the reducing sugar, and the acidity of the former are relatively small compared with the corresponding amounts obtained with fermented wines. A. F.

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